Synthesis of new optical sensors for determination of pH and chloride ions in reinforced concrete

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Dissertation

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W. Grahn, P. Makedonski, J. Wichern, W. Kowalsky, S. Wiese - "Fiberoptic sensors for an in-situ monitoring of moisture and pH value in reinforced concrete", The Third International Workshop of Structural Health Monitoring, Stanford University, 12-14.09.2001, Chapman & Hall 2002,564-574.

M. Brandes, P. Makedonski, H.-H. Johannes, S. Wiese, W. Kowalsky and W. Grahn† - "Fiberoptical Sensors in Concrete", 11 ITG/GMA-Fachtagung „Sensoren und Mess-Systeme 2002", Ludwigsburg, 03. 2002

M. Brandes, H.-H. Johannes, W. Kowalsky, P. Makedonski, J. Wichern, S. Wiese, W. Grahn - "Fiberoptical In-situ evaluation of corrosion processes in reinforcement concrete", First European Workshop on Structural and Health Monitoring-Paris-ENS Cashan, France, 10-12.07.2002, DEStech Publications 2002, 599-606.

P. Makedonski, M. Kussler, H.-H. Johannes, W.Kowalsky - "Neue Konzepte für faseroptische Chloridsensoren in der Bauwerksüberwachung", GESA Symposium Braunschweig,12-13.06.2003, VDI Verlag Gmbh-Duesseldorf 2003,167-174.

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I want gratefully to acknowledge financial support by the SFB 477, Germany.

To my family

List of abbreviations

Cl^- ISE	chloride ion selective electrodes
ISC	ion–selective carriers
EG	Ethylen glycol
TDSBC	tetrachlorodialkylsulphoalkylbenzimidazolocarbocyanine
PVA	poly(vinyl alcohol)
PVB	poly(vinyl butyral)
PVA *co*–PE	poly(vinyl alcohol *co*–ethylene)
FC	Flash chromatography
AIBN	Azo-bis-isobutyronitril
EDPA	Ethyldiisopropylamine
DPPF	Diphenylphosphinoferocene
DBPB	2-(Di-*t*-butylphosphino) biphenyl
PPA	poly phosphoric acid
ICI	anilinovinyl or anilidovinyl compounds
RSE	resonance stabilisation energy
RP	reverce phase
CT	charge transfer
PrOH	Propanol
LG	leaving group

1. Introduction

1.1. Concrete structures

1.1.1. Overview

Concrete structures such as social buildings, bridges, walls and numerous others are of great economic importance in every industrial nation. The structures in use today, require growing attention in the fields of preservation, restoration and new utilisation. The costs of these precautionary measures are increasing enormously. For example in Germany they are estimated to range from 150 to 225 billion € per year.[1, 2] The trends of financial resources invested in new buildings compared with the costs needed for preservation and rehabilitation of the existing ones show drastic tendencies worldwide. The statistics in Germany (Fig. 1–1) for the last 25 years show that in 1977 about 80 billion € were invested for new buildings and less than a quarter of that amount for renovation. In 1995 the relation is less than a half and the trends in the near future indicate that the investments for maintenance will exceed those for new constructions soon.

The structures of reinforced concrete are exposed to a variety of damaging influences, which can be of physical or chemical nature. Chemical substances, which cause damage, are numerous. They are of natural or industrial origin and occur in the soils, water and in the air. The industrial development during the last century caused increased amounts of emissions of exhaust fumes like CO_2, N_xO_y and SO_2. Thess facts lead to the necessity of prevention of deterioration of concrete constructions. In agreement with this is the statistics of highway and railway bridges in Japan in the period from 1915 to 1995 (Fig. 1–2). Thus, the maintenance and the preservation of concrete structures are of major interest.

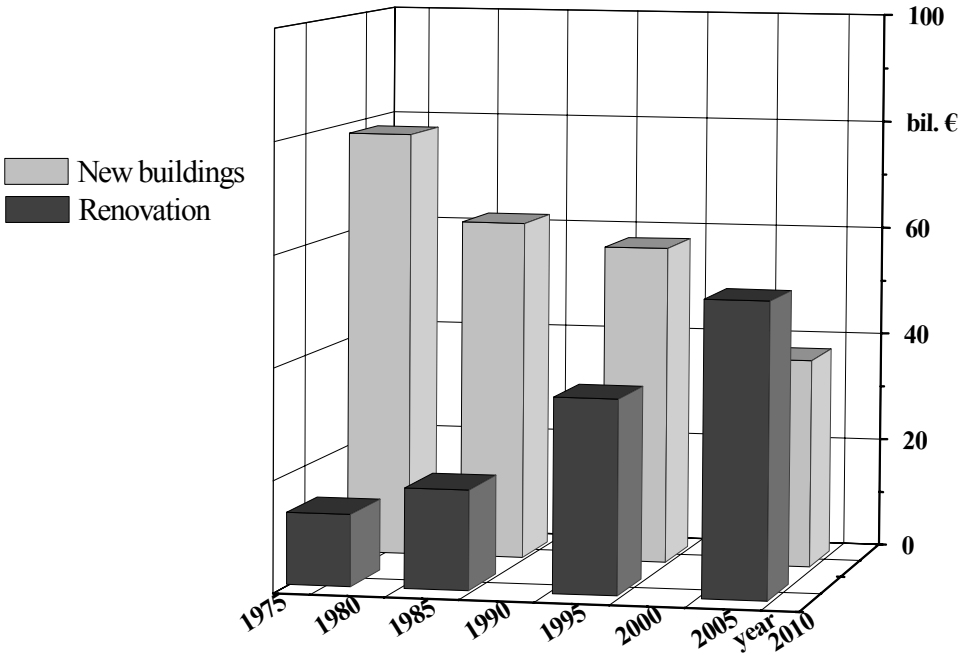
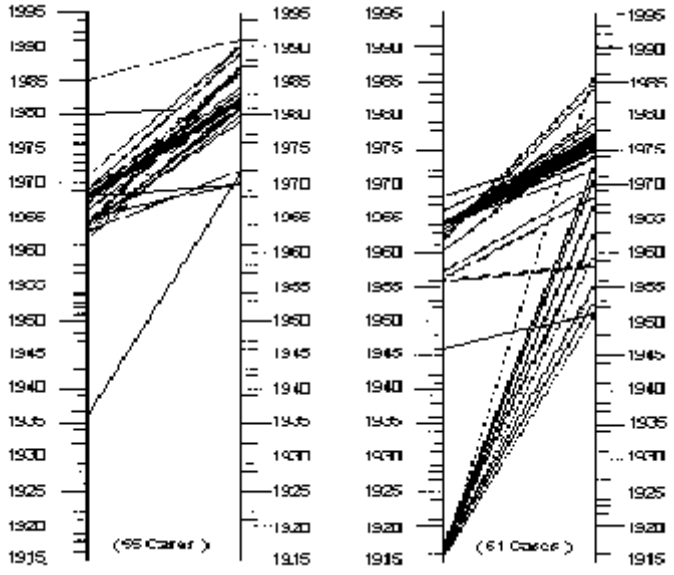


Figure 1–1: Development of construction investments in Germany



Completion year | Detection year | Completion year | Detection year

a) Railway bridges in Japan b) Highway bridges in Japan

Figure 1–2: Relation between completion and damage detection year for bridges in Japan

1.1.2. Physical and chemical properties of the reinforced concrete and corrosion attack

Concrete is an extremely durable material. Typically, it is an inhomogeneous porous material, the pH of which is in the range from 11 to 13. This high value is due to the hydration of the calcium silicates and subsequent release of calcium, sodium and potassium hydroxides into the pore liquid. In reinforced concrete this alkaline environment causes formation of an inert surface layer on the steel, which protects it against corrosion. In particular, the moisture has an important influence on the lifetime of concrete structures. Moreover, water acts as transport medium for ions, which cause damage in the concrete structures such as chloride, sulphate and carbonate. As a chemical agent the water mobilises corresponding acids from their salts. It can be accepted as a general rule that acids are the main reason for concrete damage. They dissolve the more soluble constituents of the set cements, destroying its crystalline structure and leaving only an incoherent residue. Mineral acids such as hydrochloric, sulphuric, nitric and phosphorus acids, which are produced and used in large amounts, present serious risks of contamination in the soils and water. In principle, they occur accidentally, as the result of spillage or leakage, but unauthorised waste disposal is also a source of contamination. Only sulphuric acid may occur naturally in the soil and in ground water, due to the oxidative weathering of certain sulphide minerals, chiefly the iron disulphides pyrite and marcasite (FeS_2). In the presence of air (oxygen) and moisture (water), pyrite is oxidised to ferrous sulphate and sulphuric acid:

$$2\ FeS_2 + 7\ O_2 + 2H_2O \rightarrow 2\ FeSO_4 + 2\ H_2SO_4 \qquad (1\text{–}1)$$

$$4\ FeSO_4 + O_2 + 2\ H_2SO_4 \rightarrow 2\ Fe_2(SO_4)_3 + 2\ H_2O \qquad (1\text{–}2)$$

$$7\ Fe_2(SO_4)_3 + FeS_2 + 8\ H_2O \rightarrow 15\ FeSO_4 + 8\ H_2SO_4 \qquad (1\text{–}3)$$

An example is the marsh, or lowland moor, around Osnabrueck in Germany, where the peat soil contains up to 17 % of pyrite and free sulphuric acid has been found in the ground water in amounts as large as 80 mg/l.[3]

Organic acids often have their origin in nature. They occur in living plants and as decomposition products of vegetable and animal matter. Generally, the amounts present in the soil and water are small, but under certain conditions the amount of acids can accumulate to a significant degree. Besides the deterioration of cements, the acids also cause the so–called “electrochemical corrosion” of reinforced steel. That process can proceed only at pH–

values lower than 9, because of the destruction of its protective oxide layer and its deposition in incoherent form.

In summary, the acid attack leads to a decrease of pH during the projected lifetime of concrete structures. That process is generally considered as the substantial reason for concrete deterioration and pH observation is of great interest in order to monitor acidic attacks.

Principally, the corrosion of steel in concrete is an electrochemical process. Due to local compositional or structural variations, some areas become positively and others negatively charged, and electrical cells are set up. The anodic (eq. 1–4) and the main cathodic (eq. 1-5) reactions can be written as:

$$3\ Fe + 8\ OH^- \rightarrow Fe_2O_3 + FeO + 4\ H_2O + 8\ e^- \qquad (1–4)$$

$$4\ e^- + 2\ H_2O + O_2 \rightarrow 4\ OH^- \qquad (1–5)$$

At the anode surface, ionic iron is dissolved and oxide anions are deposited. Electrons move from anode to cathode within the metal, and OH^- ions travel from cathode to anode through the pore liquid, with which it is in contact. For these processes to occur, a permanent source of oxygen (air) is needed, and the surface of the metal must remain wet. If the pH is above 11.5 and Cl^- is absent, the oxide is deposited as a thin protective film and the rate of attack is so slow as to be insignificant.[4] The chloride ions cause local breakdowns of the passivation film even at high pH. The exposed areas of metal react as anode and unaffected areas as cathode. The quantity of chloride, which has been introduced by the precursor materials during concrete production is limited and lies below the corrosion–inducing limit value. The corrosion of the reinforcement can therefore be initiated only by chloride penetrating the concrete from the outside. The risk of chloride–induced corrosion increases with easiness of migration of those ions and with the ratio of Cl^- to OH^- in the pore solution. Diffusion coefficients have been measured for alkali salts and they were larger than $1.4–3.3\times10^{-12}$ m^2s^{-1} (for alkali ions), especially if Ca^{2+} or Mg^{2+} were the counter ion.[5] The activation energy was reported to be 50 $kJ\cdot mol^{-1}$.[6] The critical chloride concentration was specified to be 0.05 M, but in some cases it could reach up to 0.5 M.[7] Usually, the chloride concentration is measured by eluting a specimen of concrete with water followed by quantitative analysis.

To the best of our knowledge there is no information available about non-destructive methods for measurement and monitoring of chloride ion concentration in concrete structures.

1.2. Fibre–optical sensors

Fibre-optical sensors are well known for more than thirty years.[8–10] Nowadays, more than 90 % of telecommunication technologies use optical fibres. Their great advantages over copper wires are very low losses of the signal over long distances and capability of fast transmission of data, which tend to reach about 20 Gbits/s per fibre.

There are two types of sensors. In the so-called instrinctic ones the fibre is directly used as a sensor.[11, 12] The second type is called extrinsic sensors, where the fibre guides the light to a sensor probe.[13, 14] The devices, based upon the second method are the so–called *optodes*. Their main advantages are:

- Durability under extreme environmental conditions and high resistance against chemical attack
- Low optical losses in the fibre over long distances
- Small size for integration of many sensor–probes in one sensor head
- No galvanic connections between sensor and analytical unit
- No interference with electromagnetic fields
- High flexibility and trouble–free behaviour
- Low costs

The principle set up of a fibre-optical sensor is shown in Fig 3–1:[15]

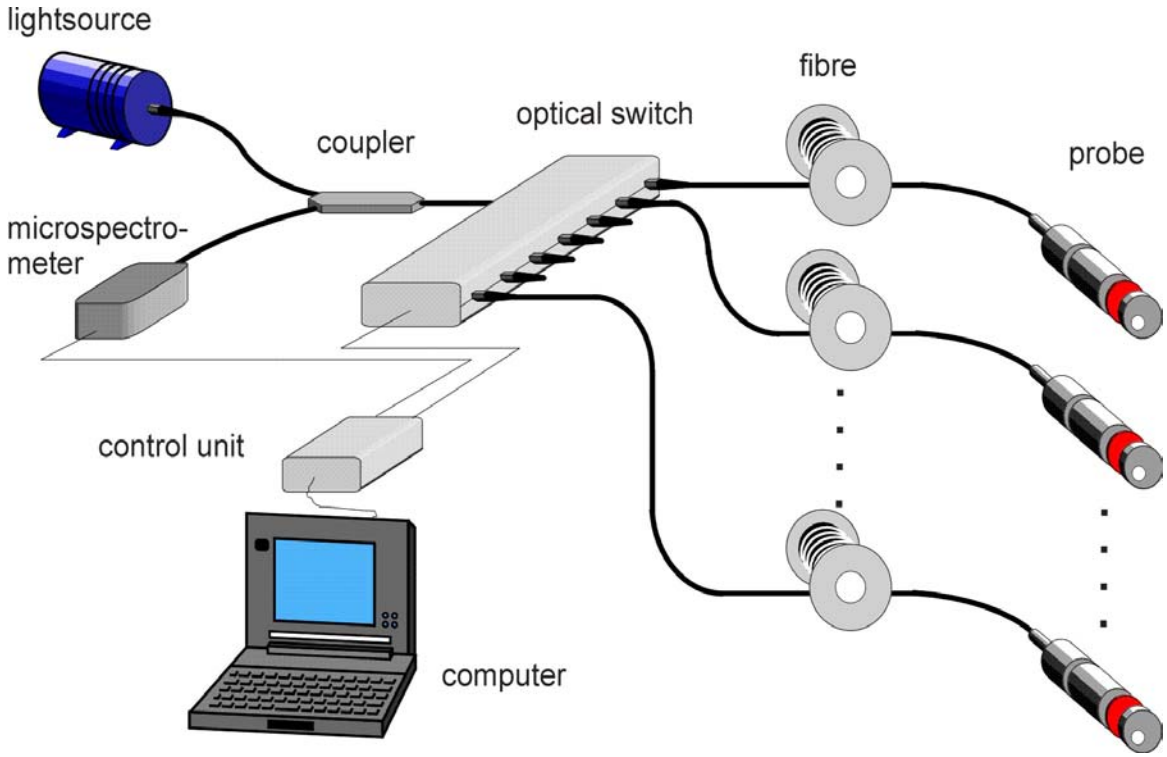


Figure 1–3: The components of an integrated fibre–optical sensor

As a light source a halogen lamp is used with a continuous spectrum extending into the visible range. The light is guided to the probe and transmitted through the sensor with characteristic optical properties. Then the signal is reflected by a mirror, coupled through a 3dB–coupler and analysed by a microspectrometer. For monitoring of a number of sensors with one spectrometer a fibre-optical switch is used, which handles up to nine different fibre channels.

1.3. Indicator materials

Generally, the probe of an optical sensor consists of an indicator material - an indicator dye, which is incorporated into an appropriate polymer. The optical properties of the dye, i.e. refraction, absorption or fluorescence are influenced by various conditions. As a consequence, the light will be changed in intensity, phase or polarity. These optical changes are easily detected by a spectrometer.

1.3.1. Indicator dyes

1.3.1.1. pH Indicator dyes

The pH is a very important characteristic of solutions of many substances. There are many different methods known for its determination, *e.g.* the pH–dependent electrical potential differences within glass electrodes[16] or the photometrically determined changes of the vis–absorption[17] and fluorescence[18] of appropriate indicator–dye molecules. The most often used indicator dyes in the spectrophotometry units are called *acid–base indicators*. An acid–base indicator is a weak acid or a weak base. The undissociated form of the indicator HIn (*e.g.* an acid) has a different colour than the ionogenic form In^- (conjugated base) of the indicator (eq. 1–6). An indicator does not change its colour from pure acid to pure base at specific hydrogen ion concentration, but rather, the colour change occurs in a range of hydrogen ion concentrations. This range is termed as the *colour change interval* and it is expressed as a pH–range.

$$HIn + H_2O \rightleftharpoons H_3O^+ + In^- \qquad (1–6)$$

Different dyes are changing their colour at different pHs. Figure 1–4 shows a number of common acid–base indicators and their colour changes.

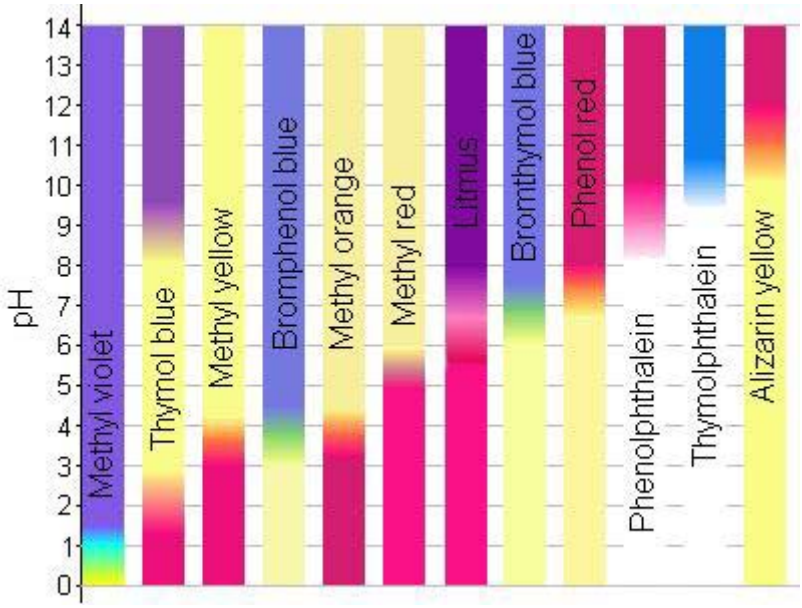
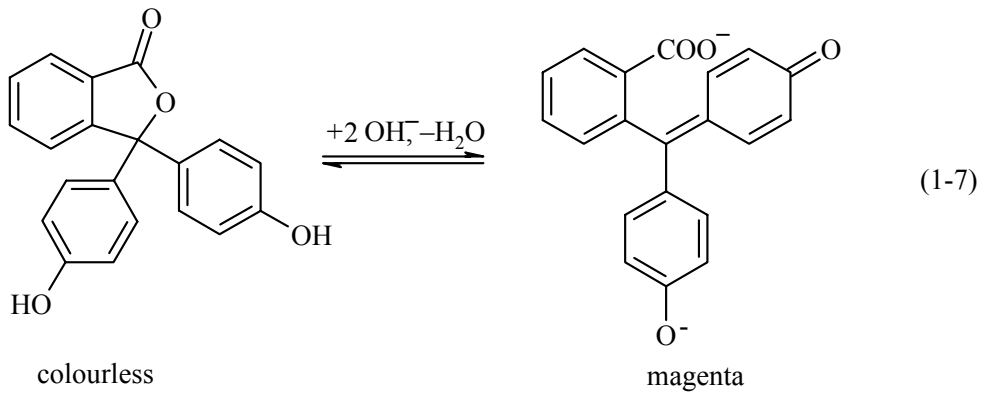


Figure 1–4: pH– indicator dyes and their colour change

As can be seen from Figure 1–4, the acid–base indicators can be generally divided into two major classes of chemical substances: the group of triarylmethane dyes (Methyl violet, Thymol blue, Bromphenol blue, Methyl red, Bromthymol blue) and the group of azo dyes.
One of the most widely used triarylmethane indicator dyes for the alkaline region is phenolphthalein (eq. 1–7):



(1-7)

The dye is colourless in acidic solutions and the colour changes from pink to magenta at pH>8.5. The colour change is easily recognisable by the human eye, but phenolphthalein is not appropriate for fibre-optical detection. The first disadvantage is, that the dye becomes again colourless at pH values higher than 12–12.5. Furthermore, it is not possible for such

sensor to be calibrated, because there is no internal reference, in other words the signal difference appears only by changing the absolute intensity in the absorption maximum. The increase or decrease of the signals absolute intensity is prone to misadjustments between the fibre and the sensitive material or due to internal disruptions. However, this dye is a standard indicator used by engineers to check the pH in reinforced concrete. Yet for early and precise diagnostics phenolphthalein is not applicable.

For exact and reliable measurements an internal reference is necessary. Some acid–base indicators show an *isosbestic point* of constant absorption.[19, 20] This point is independent of the pH. Other internal reference is the relation between two absorption maxima. When only one is available bathochromic or hypsochromic shifts under different conditions are required (*e.g*. Reichardt`s dye by polarity changes).

Azo dyes are compounds, which contain at least one azo group (–N=N–) connected to sp^2-hybridized carbon atoms. They have not been found to occur in nature. The first azo dyes were produced by C. Mene in 1861 (Aniline Yellow)[21] and by Martius in 1863 (Bismark Brown)[22], prior to the discovery of the diazotisation reaction and of diazo compounds by P. Griess in 1858.[23] The parent compound is diazobenzene. It was obtained by Mitscherlich in 1834 and formed by the action of alcoholic caustic potash on nitrobenzene.

With regard to the number of the azo groups present, the dyes are called monoazo (containing one azo group), bisazo (two azo groups), tris, tetrakis and so on.

The azo dyes are classified as anionic-, disperse-, azoic-, cationic-, complex-forming, direct- and reactive azo dyes and azo pigments depending on their physical–chemical properties and uses in industry.

Hydroxyaryl azo dyes are another important group of acid–base indicators for the alkaline pH range. The common acid–base equilibrium is shown in eq. 1–8.

$$\mathrm{Ar–N{=}N–Ar'OH} \overset{+OH^-,\ -H_2O}{\rightleftharpoons} \mathrm{Ar–N{=}N–Ar'O^-} \qquad (1\text{-}8)$$

where Ar and Ar' are aromatic or heteroaromatic residues, Ar contains an acceptor group, and the OH–group is on ortho– or para–position. Their advantages are:

- Both acidic and conjugated basic forms are coloured
- Possess very good chemical stability
- In many cases they have an isosbestic point
- Can be synthesised by simple chemical reaction

• Able to bear different functional groups

1.3.1.2. Chloride selective indicators

The determination of the chloride concentration is of great interest in analytical chemistry. It is the major extracellular anion in whole blood and serum in the human body, where its concentration reaches 98–110 mM.[24] Chloride is also the predominant balancing anion in the inorganic salts in seas and oceans.[25] Various methods have been developed for the determination of its concentration. Chloride ion selective electrodes (Cl^- ISE) were reported, based on potential differences.[26–28]

A wide range of optical ion sensors has been developed for photometric determination. Most of them are based on the mechanism of co–extraction.[29–31] These sensors are composed of carrier molecules, pH indicator dye and ionic additives, incorporated in a plasticized poly(vinyl chloride) (PVC) membrane. Ion–selective carriers (ISC) extract the analyte from the sample solution into the polymeric bulk membrane. In order to maintain electroneutrality of the membrane, protons (H^+) are co–extracted. That is optically transduced by a lipophilic pH indicator (In) dye (Fig. 1–5).

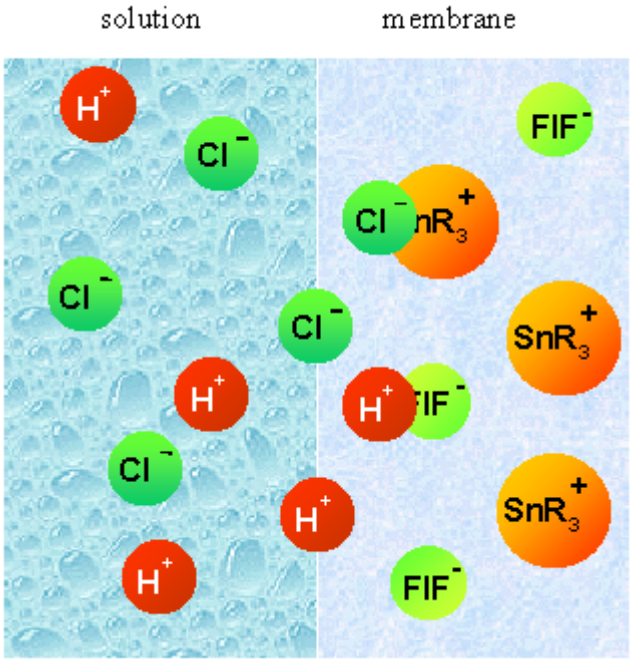
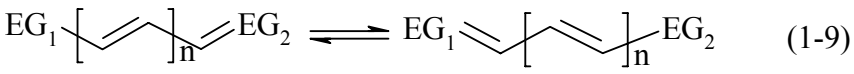


Figure 1–5: Principle of co–extraction by optical detection of chloride ions(FlF^- = fluoresceine derivative, SnR_3^+ = chloride selectophore)

The main limitation of this approach is the cross–sensitivity to the pH, which depends on the pK_a of the indicator dye.

Another important class of optodes is based on a quenching effect of the luminescence of certain heterocycles[32, 33] or polarity–sensitive dyes, containing quaternary nitrogen atoms.[34] Unfortunately, all these methods fails in the case of pH higher than 9.[32, 34] It could be due to the similar properties of the hydroxide anion or to the destruction of ion–selective parts of the indicating molecules. Up to now chloride selective indicator dyes for high alkaline environment are unknown.

Polymethine dyes nowadays include a huge number of coloured organic compounds. Practically, they cover all shades from yellow to green. As far as known, C. H. Williams was the first chemist who came across a prototype polymethine dye (1856).[35] This dye was of "magnificent blue colour" and therefore it was called *cyanine* (cyanos $_{(Greek)}$ = blue). The common cyanine structure is shown in eq. 1–9.



(1-9)

Where EG_1 and EG_2 are end groups, which are hold together by a methine chain, where $n = 0, 1, 2\ldots$ The end groups can be of carbo– or heterocyclic or acyclic structure. When $EG_1 = EG_2$ the dyes are called symmetric polymethines and respectively asymmetric, when both end groups are different. The dyes can be cationic (cationopolymetines), anionic (anionopolymethines) or neutral (neutropolymethines).

With regard to n they are named monomethines ($n = 0$), trimethines ($n = 1$), pentamethines ($n = 2$) and merocyanines when n is not a even number.

The phenomenon of aggregation of polymethines was discovered by Scheibe[36] and by Jelley.[37] A large number of polymethine dyes form either in solution or adsorbed on the surface of ion crystals loosely bonded dimers and molecular complexes containing variable numbers of molecules.

Their *J*–aggregation is a reversible process depending on temperature and dye concentration. Salt effects and solvent polarity can also influence it.[38] Within these aggregates the separate molecules are hold together by non–covalent bonds (Fig. 1–6).

The *J*–aggregation of polymethine dyes adsorbed on silver halides is great of importance in spectral sensitisation of photographic emulsions. Further application is in various optical information storage devices.[39]

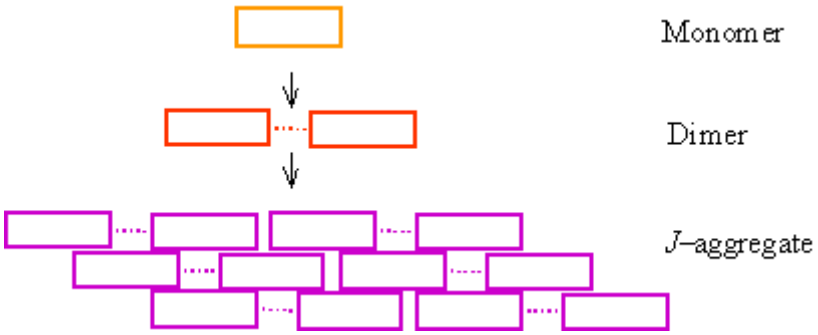


Figure 1–6: Principal Scheme of *J*–aggregation (simplified)

It is known that *J*–aggregation of tetrachlorodialkylsulphoalkylbenzimidazolocarbocyanine (TDSBC) occurs in alkaline environment.[40,123,146] Other authors have reported that polymethine dyes formed aggregated structures by interaction with NaCl aqueous solutions.[41] It remains unclear whether it would be possible to combine both properties in a single cyanine molecule. The answer of this question is sougth in the present work.

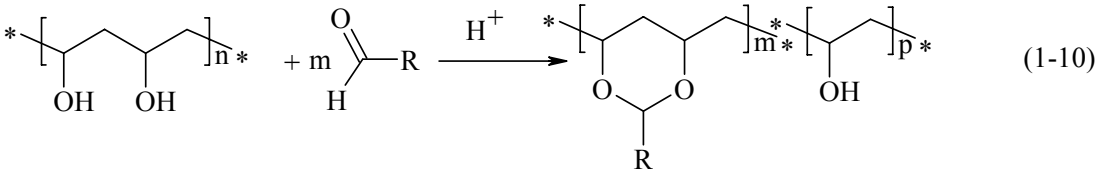
1.4. Polymer support

The optodes in fibre–optical systems consist of composites of dyes and transparent polymers. The dyes are usually incorporated in the polymer by two general methods: either as host-guest system or by covalent bonding. The first method is quite straightforward, but it suffers from dye aggregation and leaching, especially when pH–indicator dyes are used. This is overcome by using the second approach. Several methods for the preparation of dyes covalently bonded to the polymer backbone are available: either by co–polymerization of functionalised dye–monomer and the corresponding co–monomer[42, 43] or by bonding of dyes to the polymer using suitable functional groups.[44, 45]

Different polymers are used as dye carriers for this type of sensor. They have to fulfill several requirements like transparency within the vis–range and a sufficient hydrophilicity to render possible an interaction of the indicator dye and the sample. Wolfbeis *et al.* used polyester coated with cellulose acetate and have bonded vinylsulphone azo dyes by ether linkages to the hydroxy groups of cellulose.[46] The sensors produced in this manner exhibit fast response times and sufficient stability at pH range from 12.0 to 12.5, but they are restricted to short–

term measurements. pH–sensitive membranes based upon highly lipophilised dyes absorbed on the surface of plasticised PVC have been reported.[47] Other authors have proposed the immobilisation of a pH–sensitive dye by using ion–exchangers.[13] In the first case leaching of the dyes is the main problem and makes these systems useless for long–term applications. The second method has advantages, since the dyes are immobilised by means of strong electrostatic interactions. Hence, the sensors show fast response and leaching is not observed. On the other hand the dyes are charged, which results in a number of other shortcomings.

Acetal formation using the hydroxyl groups of the polymers (*e.g.* poly(vinyl alcohol)) and formyl groups of different aliphatic aldehydes are known since 1924, yielding poly(vinyl acetal) resins.[48, 49] The poly(vinyl alcohol) (PVA) **1** reacts as a 1,3–diol with aldehydes **2** to form cyclic acetals **3**:



1 **2** **3** (1-10)

The reaction of producing poly(vinyl acetals) **3** is shown in eq. 1–10, where n, m and p can vary over a wide range. The reaction is reversible and acetal rubbers with more than 80 % acetalisation are unknown. The most important commercially produced acetal rubbers are poly(vinyl formal) and poly(vinyl butyral).

Two types of methods have been described for use of PVA in optical sensors:

In the first one the dye is dissolved in an aqueous solution of PVA and the polymer was crosslinked with glutaric aldehyde.[50] The sensor material is then attached to the tip of an optical fibre, as long as its viscosity allows it.

The second approach involves the use of cyanuric chloride.[51] However, the authors report side reactions affecting the sensorically important functionality of the dyes and hydrolysis of cyanuric chloride during attempted coupling reactions with aqueous solutions of PVA.

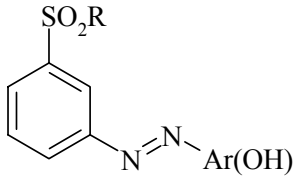
For our purposes acetals have very favourable properties. The acetal linkage possesses extremely high stability under basic conditions. Acetals are widely used in industry, but to our knowledge - to bind a dye as an acetal to the PVA has not been reported yet.

2. Aims and Purposes

The aim of this study was to develop and investigate indicator dyes for fibre- optical *in situ* monitoring of chemical species, which give rise to corrosion processes in reinforced concrete. The indicator dyes must be incorporated into suitable polymers, which allow a long–time reversible functionality of such prepared sensor materials. The chemical species, which cause deterioration of concrete structures by electrochemical corrosion of reinforced steel, are acids and chloride ions.

Our first goal was the synthesis and development of pH–indicator sensors. The acidic attack should be monitored with these pH–indicator dyes at the high alkaline end of the pH scala. For this purpose pH–indicator dyes have to change their optical properties (absorption) in the range form 12.5 to 10.5 with respect to pH of the concrete structures. As a result the invention of an early warning system would be possible. It will allow detection of the acidic attack at an early stage.

Hydroxyazo dyes are suitable for pH determination in the alkaline range, as mentioned in section 1.3.1.1. With respect to monitor the colour change of the indicator dyes in the high alkaline pH-ranges, we have chosen the following general structure:



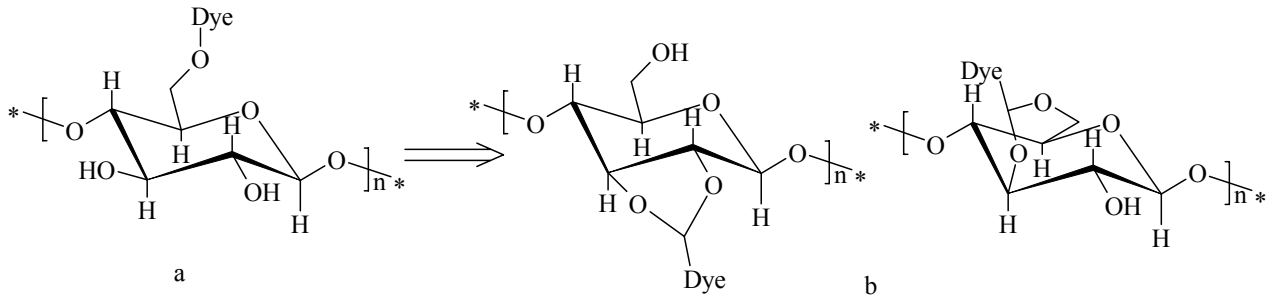
4

Figure 2–1: General structure of synthesised pH–indicator azo dyes **4**

In Figure 2–1 R is a carbon chain with a reactive group, which can act as spacer link between the dye and the polymers and Ar is an aromatic system (phenyl, naphthyl, or anthranyl nucleus). The *m*–position of the sulphone group to the azo–functionality was chosen, because in this case conjugation with the chromophore chain is not desirable. The task was to synthesise dyes, which are weak acids. The deprotonation of these weak acids will require a

higher concentration of hydroxide anions, and, hence, the colour change will take place at higher pH.

Numerous pH–indicator dyes are known, which have found an application in analytical chemistry. The dyes have been incorporated into the solid supports (mainly polymers) by two methods: as host–guest systems or by covalent bonding of the dye to the polymer backbone or glass surface. The second method is more reliable for pH–indicator dyes, because they interact with the acids/bases through a protonation/deprotonation mechanism and in this case exist as ions, which are water–soluble very well. The covalent linkage of the dyes prevents their leaching from the solid support. Dyes, which are capable to react with other substrates and, as a result, create a new covalent bond between them, are called reactive dyes. In order to prepare stable pH–indicator sensor all three parts of the sensor body: the indicator dye, the polymer and the spacer link, must be stable for a long period of time: in the range of decades. The known methods are based on an ether linkage of the reactive vinylsulphonyl dyes with the hydroxyl groups of cellulose, obtained through hydrolysis of its acetic esters (Scheme 2-1, a).[45 a]



Scheme 2–1: Ether (a) and acetal (b) linkage of the indicator dyes to the cellulose substrate

The cellulose layer was prepared as a thin film on a polyester support. This resulted in very fast response time, but the sensors showed short–time stability. The continuous hydrolysis processe in the cellulose acetate converted it to cellulose, which absorbed a large amount of water and was hence unstable on the polyester support. Whitin a week the sensor had been destroyed.

Our aim was to extend this approach by creating an acetal spacer link between the polymer and the pH–indicator dye (Scheme 2–1, b). The acetal functionality is extremely stable under alkaline conditions and can be considered as a double–ether linkage. That mode could extent the use of polymers to all polyhydroxyl–containing macromolecules. It is very difficult to work with cellulose, because of its insolubility in common organic solvents, furthermore it

could be a target for bacterial attack. For this reason it is not suitable for the preparation of fibre- optical sensors.

Another polyhydroxyl polymer is poly(vinyl alcohol) (PVA). Its hydroxyl groups are in 1,3-alternation and consequently suitable for acetalisation with aldehydes. The corresponding poly(vinyl acetals) are known and produced in industry.[78–79] To the best of our knowledge, the acetalisation of a PVA with dyes has been not reported until now.

Our aim for pH–indicators was to synthesise and investigate a new class of reactive dyes, containing a reactive aldehyde group. The dyes were to be linked to the PVA and its *co*-polymers by an acetal functionality. Such prepared sensors could be suitable for fibre-optical measurements of the pH.

The known optical chloride sensors are restricted to the neutral pH–range.[29–34] As mentioned above (section 1.1.2.), the chloride ions caused electrochemical corrosion even in high alkaline environment in reinforced concrete. The dyes under study can be classified into three groups:

1. Polymethoxyacridones **5** and quaternised polymethoxy acridines **6**, the fluorescence of which should be selectively quenched by the chloride ions. That optical signal should be independent of the hydroxide ion concentration.

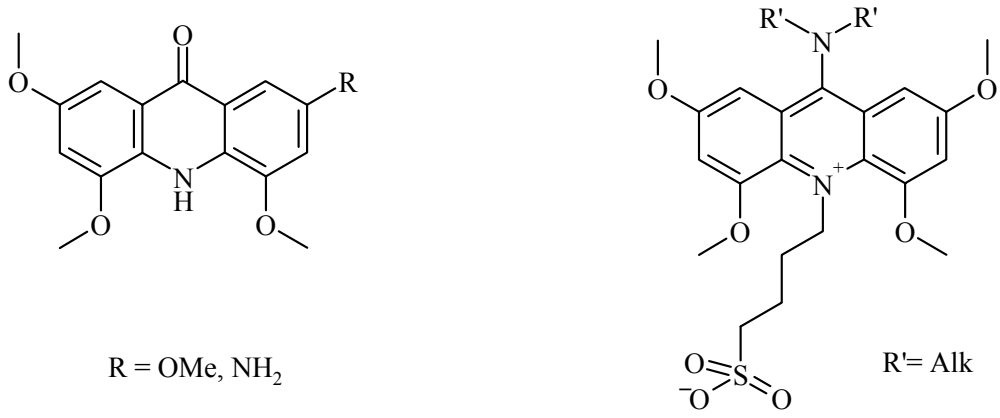
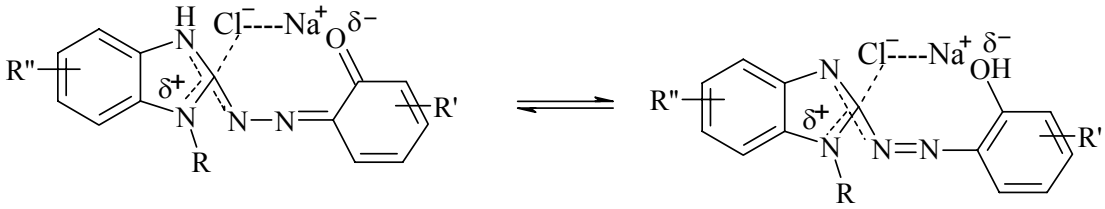


Figure 2–2: Fluorescence–optical sensor materials for determination of chloride ions

The methoxy groups are conjugated with the nitrogen atom of the heterocyclic ring and decrease its electron–withdrawing power. This should prevent quenching by the hydroxide ions. Wolfbeis *et al*. have reported the application of fluorescence quenching of quaternised quinolines and acridines by chloride ions.[32, 34] However, at pH higher than 9 the fluorescence was quenched by hydroxide ions as well.

2. Complex–forming benzimidazolo azo dyes **7**, based on the guanidinium moiety (Fig. 2–3).



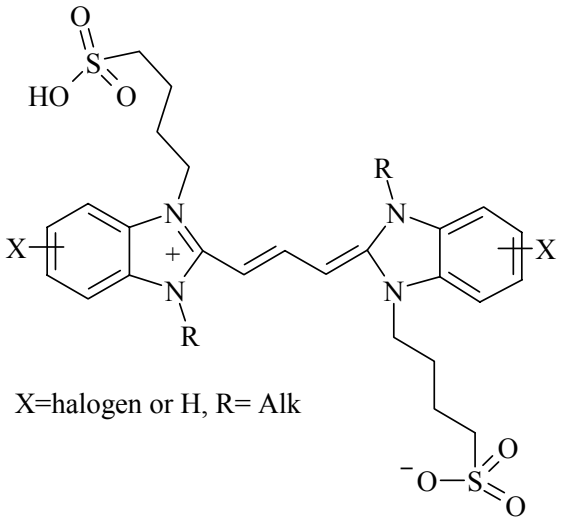
R, R', R" = Alk.

7

Figure 2–3: Complex–forming 2-azo benzimidazole dyes **7**

This approach is based on complex formation of the guanidine ion with anions.[129] The guanidinium moiety is available in 2-azo benzimidazole dyes **7**. This sensor part is conjugated with the chromophore chain of the azo dye. The formation of the complex should result in changes of its absorption spectrum. Both hydroxy azo and ketohydrazono tautomers are able to take part in complex formation.

3. *J*–aggregation of bisbenzimidazolotrimethine dyes (Fig. 2–4).



8

Figure 2–4: General formula of bisbenzimidazolotrimethines **8**

It is known that trimethine dyes form *J*–aggregates under to the influence of different salts, solvents and in alkaline media (hydroxide ions).[40–41] Our aim was to synthesise and to investigate the properties of bisbenzimidazolo trimethines **8** and especially their aggregation

behaviour at high pH in the presence of NaCl. Their advantage is the high symmetry of the molecule, which should facilitate aggregation. The benzimidazole rings impart the possibility for better delocalisation of the positive charge between both almost equivalent nitrogen atoms. That dye–class was also investigated from De Rossi *et al*.[40 a] and Pawlik *et al*.[123] The optical changes must be independent of high pH and the presence of other ions.

The chloride–sensitive dyes should be incorporated into suitable polymer matrices, where their optical changes can occur. By complex–forming of the trimethine dyes the host–guest principle could be applied, because of their large volume and water insolubility.

To the best of our knowledge, optical sensors for chloride ion determination under strongly alkaline conditions are not known yet.

3. Results and Discussion

3.1. Synthesis of pH–indicator azo–dyes

3.1.1. Synthetic methods for the preparation of azo dyes

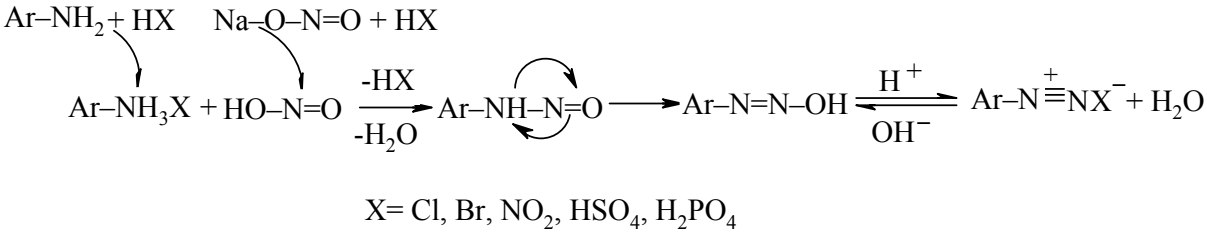
A great number of absorbancy–based pH indicators are known, but only a few have been applied for fibre–optical pH determination.[13, 51] In the basic pH–range bromphenol blue has been used.[14] Wolfbeis *et al* have reported the application of reactive azo dyes for covalent immobilisation onto cellulose.[45b] The sensors exhibit short response times, but they are unstable over long periods of time and are not suitable for pH–measurements in reinforced concrete. However, the advantages of the hydroxyazo dyes – an appropriate pKa in the alkaline pH range, strong absorption within the visible range and photo- and chemical stability, make them attractive candidates for fibre-optical applications. The improvements must concern the covalent binding of these dyes to polymers as well as enlargement of their indicator properties in the pH range from 10 to 14.

The synthesis of azo dyes generally involves the creation of the azo–group (–N=N–). There are two kinds of reactions from the mechanistic point of view - electrophilic substitutions of a diazonium salt (diazo component) with nucleophilic partner (coupling component) and condensation reactions.

3.1.1.1. Azo coupling reactions

The synthesis of azo dyes by azo coupling is an essential method. Practically all known azo dyes were prepared using this approach, only a few exceptions have been reported.

The diazotisation of an aromatic or heteroaromatic primary amine is the first step involved in building of the azo group. Usually, the amine is dissolved in mineral acidic aqueous solution, where the presence of at least 2.5 equivalents of the acid are required for smooth reaction.[52] One equivalent is required for conversion of the amine to the salt, the other is involved in the production of nitrosating agent from the respective alkali salt and the remaining half to keep the pH, necessary for the reaction, since the equilibrium in the third step demands it (Scheme 3–1):



Scheme 3–1: Mechanism of diazotisation of aromatic amines

Diazotisation is carried out at low temperatures, usually at 0 °C, because of the instability of nitrous acid and the produced diazoniuim salt. Weakly basic amines require a higher acid concentration to avoid the formation of diazoamino compounds (Ar–N=N–NH–Ar).[53] Another reason for using stronger acids is the fact that such diazonium salts are readily hydrolysable in diluted acids. Very weakly basic amines, which bear substituents with strong -I/-M effects (e.g. dinitro or polyhalogen anilines) can be dissolved and subsequently diazotised only in concentrated sulphuric or phosphoric acids.[54] The diazotising agent is nitrosyl sulphuric acid (HSO_4NO), when sulphuric acid is used.

It is difficult to dissolve amines which contain sulphonic or carboxylic acid groups in acidic media, because they exist as zwitterionic structures ($^-O_3SArNH_3^+$). Such amines are diazotised according to the so–called “indirect method”.[55] First they are dissolved in water or diluted alkali and sodium nitrite solution is added. The resulting solution is then added to the cooled acid.

There are known methods for diazotisation in non–aqueous medium by using isoamylnitrite.[56] In these cases either the amino/diazonium salt compounds are decomposed under strongly acidic conditions or other important functionalities are in danger.

The second step in the synthesis of an azo dye is the reaction of the diazonium salt and is called *azo coupling*. This reaction takes place only with substrates activated for electrophilic substitution, e.g. aromatic compounds, which carry electron–donor substituents such as OH, NH_2, NHR *etc*. The reason for this requirement is the fact that diazonium ions are relatively weak electrophiles. An electron–acceptor in the diazo component increases its electrophilicity power.

The equation, describing this process is given below:

$$Ar–N\overset{+}{\equiv}NX^- + R–H \longrightarrow Ar–N=N–R + HX \qquad (3–1)$$

Where R can also be a compound with activated methylene groups. There are two possibilities to carry out an azo coupling reaction – in acidic or alkaline medium. Aromatic amines are normally coupled in weakly acidic solutions (eq. 3–2). As a result of the coupling reaction an equivalent acid is generated. In this way the reaction solution should possesses some buffer capability. Based on the increasing electron–donor activity by deprotonation in alkaline condition phenols and naphthols are coupled at pH higher than 9 (eq. 3–3):

$$Ar–NH_3^+ \rightleftharpoons Ar–NH_2 + H^+ \qquad pK_a \text{ approximately } 4 \qquad (3–2)$$

$$Ar–OH \rightleftharpoons Ar–O^- + H^+ \qquad pK_a \text{ approximately } 10 \qquad (3–3)$$

There is also an interesting possibility for chosing the position of the azo–coupling by varying the pH of the reaction:

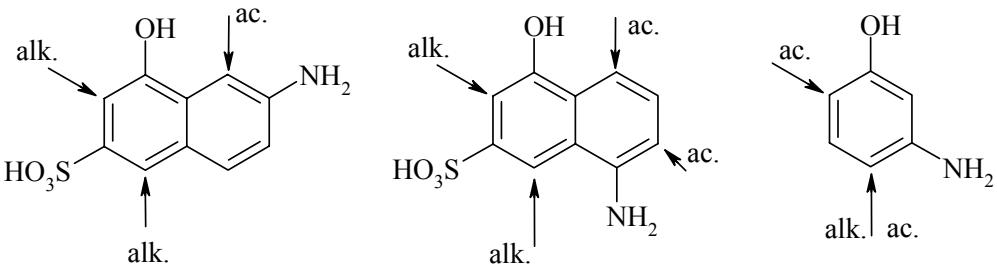
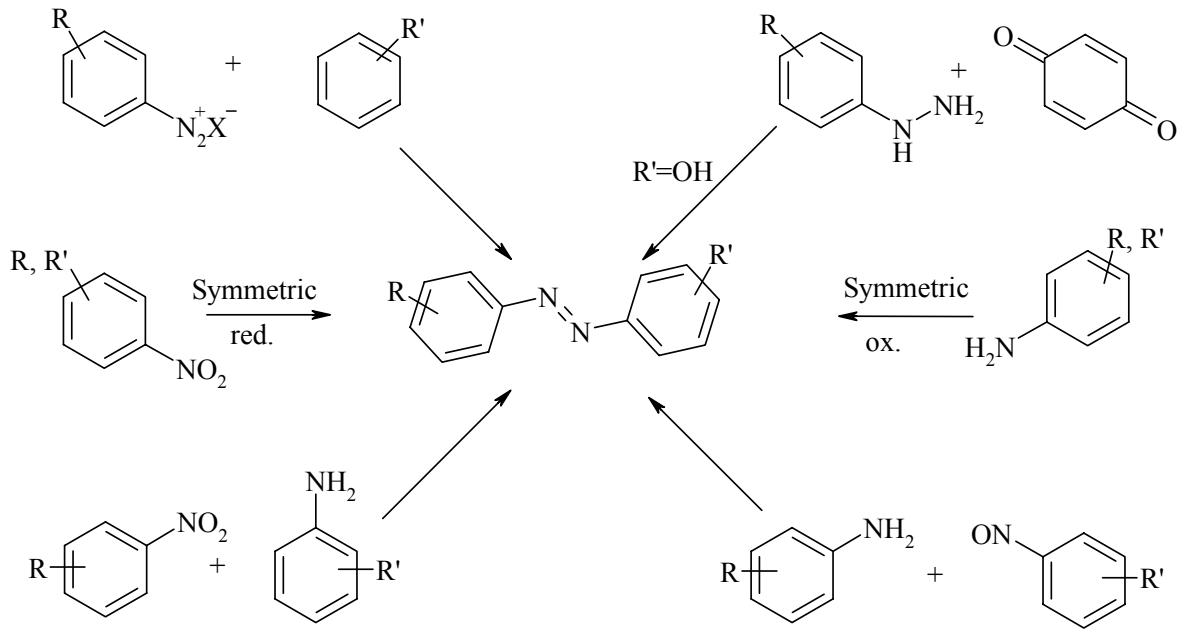


Figure 3–1: Different possibilities for azo coupling in dependence of pH of the coupling solution (ac. = acidic pH, alk. = alkaline pH)

Under alkaline conditions phenolate ions are produced, which activate the nuclei stronger by the increased positive M–effect. Under weakly acidic pHs the amino–groups control the orientation of the electrophilic attack of the diazonium ions.

3.1.1.2. Condensation reactions

The condensation reaction forming an azo dye can be divided into two types concerning the type of covalent bonds formed. In the first type a C–N bond is generated. The condensation reaction takes place between arylhydrazines and quinones, discovered by Zincke and Bindewald in 1884.[57] They found that 4–phenylazo–1–naphthol, synthesised by coupling phenyldiazonium ion with 1–naphthol, can also be obtained by reaction of phenylhydrazine with 1,4–naphthoquinone. This method is of importance for the preparation of hydroxyazo compounds, as well as for interpretation of the hydroxyazo–ketohydrazone tautomerism.
In the second approach a N–N bond is formed. Typically, these reactions take place between aromatic amines and nitroso compounds, which can be produced as intermediates during oxidative or reductive reactions.[58] Both types are limited by the substrates and have hence restricted applications.
The methods for synthesis of azo dyes are summarised in Scheme 3–2:



Scheme 3–2: Methods for synthesis of azo dyes (R, R' are common substituents)

3.1.2. Synthesis of an alkylsulphone spacer in diazo components

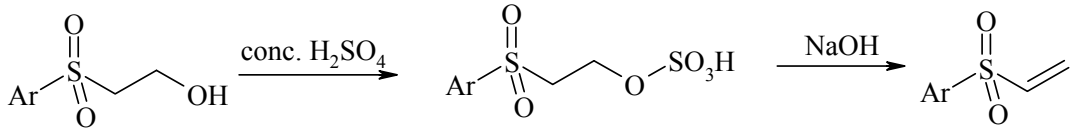
The sulphonic group is widely used in the preparation of anionic azo dyes because of its strong electron withdrawing character and readily dissociation in a wide pH range.[59] Thus, these dyes are water–soluble and exist as anions.

The substitutiton of a hydroxyl group in the sulphonic group by a carbon chain–residue produces a sulphone. The presence of that group in azo dyes decrease its water–solubility and these derivatives are called disperse azo dyes. When the carbon chain–functionality is capable to form a covalent bond with hydroxyl or amino groups from the polymer substrate the corresponding dyes are called reactive dyes and the connecting units – spacer or bridge links.[60]

3.1.2.1. Preparation of the reactive vinylsulphonyl group

Vinylsulphonyl azo dyes belong to the group of reactive azo dyes. They react by a nucleophilic addition mechanism (Michael addition).[61] In the textile industry the vinylsulphonyl group is prepared *in situ* and bound to the fibres in the subsequent stage. The

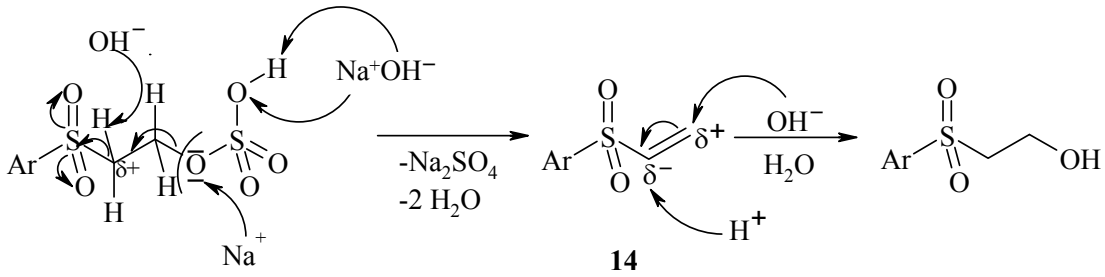
preparation of this group amounts to an 1,2-elimination of one molecule water from a β–hydroxyethylsulphone derivative **12**:



12 **13** **14**

Scheme 3–3: Introduction of a vinylsulphone group *via* sulphonoethylsulphate intermediates **13**

Wolfbeis *et al* have synthesised covalently bound azo dyes to the cellulose layer *via* vinylsulphonyl groups.[45a] For the preparation of vinylsulphones this procedure was improved by us. In this two step process (Scheme 3–3) an ethylsulphoester **13** is produced first with concentrated sulphuric acid. In the second step Na_2CO_3 is carefully added to the solution until the pH reached 5–6. This is done in order to avoid an undesired fast increase of the temperature, the volume of the solution, and the formation of foam by the carbon dioxide generated in this manner. Finally the ester is destroyed heterolytically with 2 *N* NaOH solution and the α-proton is abstracted by hydroxide (Scheme 3-4).



14

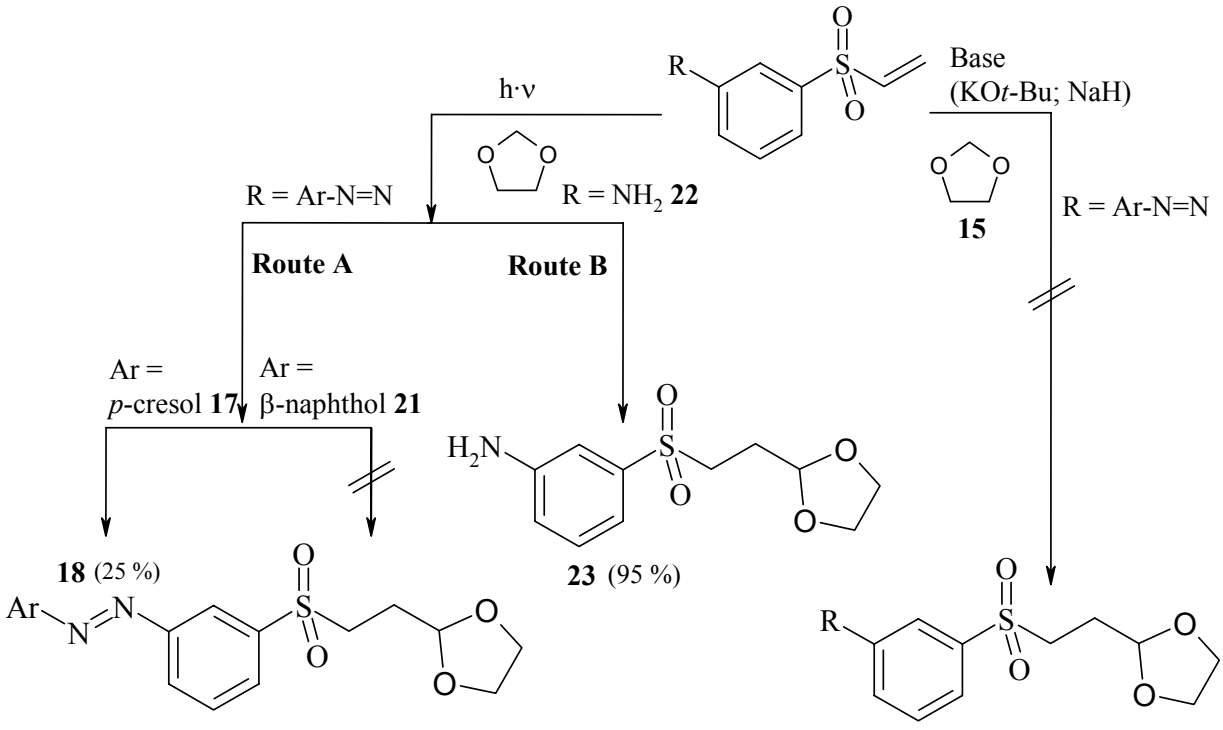
Scheme 3–4: Possible 1,2–elimination mechanism to vinylsulphone derivatives **14**

The main problems here are the undesired reverse reaction and the addition of water, a process very efficiently catalysed by the available hydroxide ion. This is overcome by immediate extraction of the formed vinylsulphones **14** from the aqueous phase with diethyl ether during the addition of sodium hydroxide solution by the following mode. The amount of ether is approximately reduced to $^2/_3$ of the volume of the aqueous acidic solution and the mixture was vigorously stirred until both phases are evenly distributed. The alkali solution is then slowly added and the temperature is maintained between 10 and 20 °C with addition of ice to the solution. The base is added until its first drop caused irreversible colour change of

the indicator dye or the pH reaches 10 in the case of aniline–derivatives. There are reports of kinetic studies about the hydrolysis of dye **20** and other vinylsulphonyl azo dyes, where pH > 12 and a temperature of 60 °C were given as conditions for Michael–addition of water to the dyes.[62] In our experiments even at low alkalinity (8 > pH > 10) and at 15 °C this reaction takes place. In this manner dyes **17** and **21** and aniline **22** were obtained in high yields (80-95 %).

3.1.2.2. Introduction of a protected carbonyl group

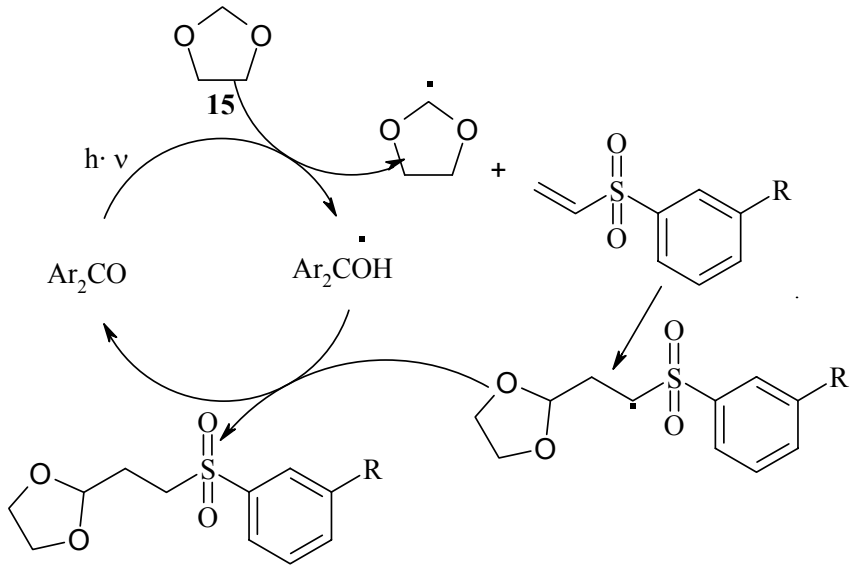
Simpkins in a review about the chemistry of vinylsulphones[63] noted their significant reactivity as Michael acceptors. In our synthetic effort we also tried to employ this method, the aim being to attach to the β–position a protected formyl group by using 1,3–dioxolane **15** as a reagent. The C - atom carries a particular positive partial charge (δ^+), thereby providing the opportunity for deprotonation. As a result a carbanion would be formed and the Michael addition can be applied. However, both experiments to deprotonate **15** using KO*t*-Bu and NaH as bases, respectively, failed (Scheme 3-5), probably because of the very low acidic character of the methylen group.



Scheme 3–5: Addition of 1,3–dioxolane **15** to vinylsulphones

Another possibility to form a protected formyl derivative is β–radical addition (Scheme 3-5). It is known that vinyl sulphones are capable of addition reactions involving carbon–centered radicals.[63] Consequently, the photochemical addition seemed to be a better choice, since AIBN is usually a source for a large number of side–reactions. Inomata *et al.* reported a successful application of benzophenone or acetophenone as photochemical sensitisers.[64] A similar method was employed for α–arylsulphinyl enones[65] and α, β–unsaturated ketones.[66] Unfortunately, by performing the reaction with the *p*–cresol azo dye **17** the yield was poor. The reaction failed completely and formation of a colourless solution was observed when the substrate was the β–hydroxynaphthyl azo dye **21** (Scheme 3–5, route A).

Better results were obtained using aniline **22** (Scheme 3–5, route B), the precursor for azo dyes. The reaction was complete in a relatively short time (5–10 min), instead of 1 hour for the dye, and the yield was almost quantitative. Obviously, the reaction with dyes was poor because of the instability of the azo–group under irradiating conditions, and failed completely with naphthol–derivatives due to ketohydrazono tautomerism. The mechanism is shown in Scheme 3–6:



Scheme 3–6: Mechanism of photochemical addition of 1,3–dioxolane to vinylsulphones

Probably, the dye as well as the used benzophenone act as photochemical sensitisers in the case of hydrazono–tautomer, and this process destroy the chormophore chain. A single

crystal of **21** suitable for X–ray structure investigation could be obtained by recrystallisation from acetone is given in Figure 3–2:

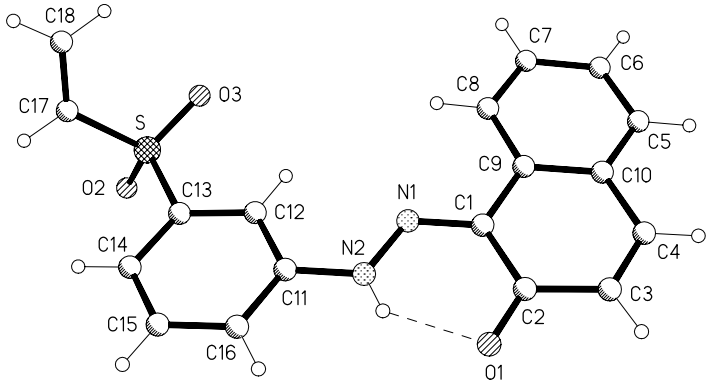
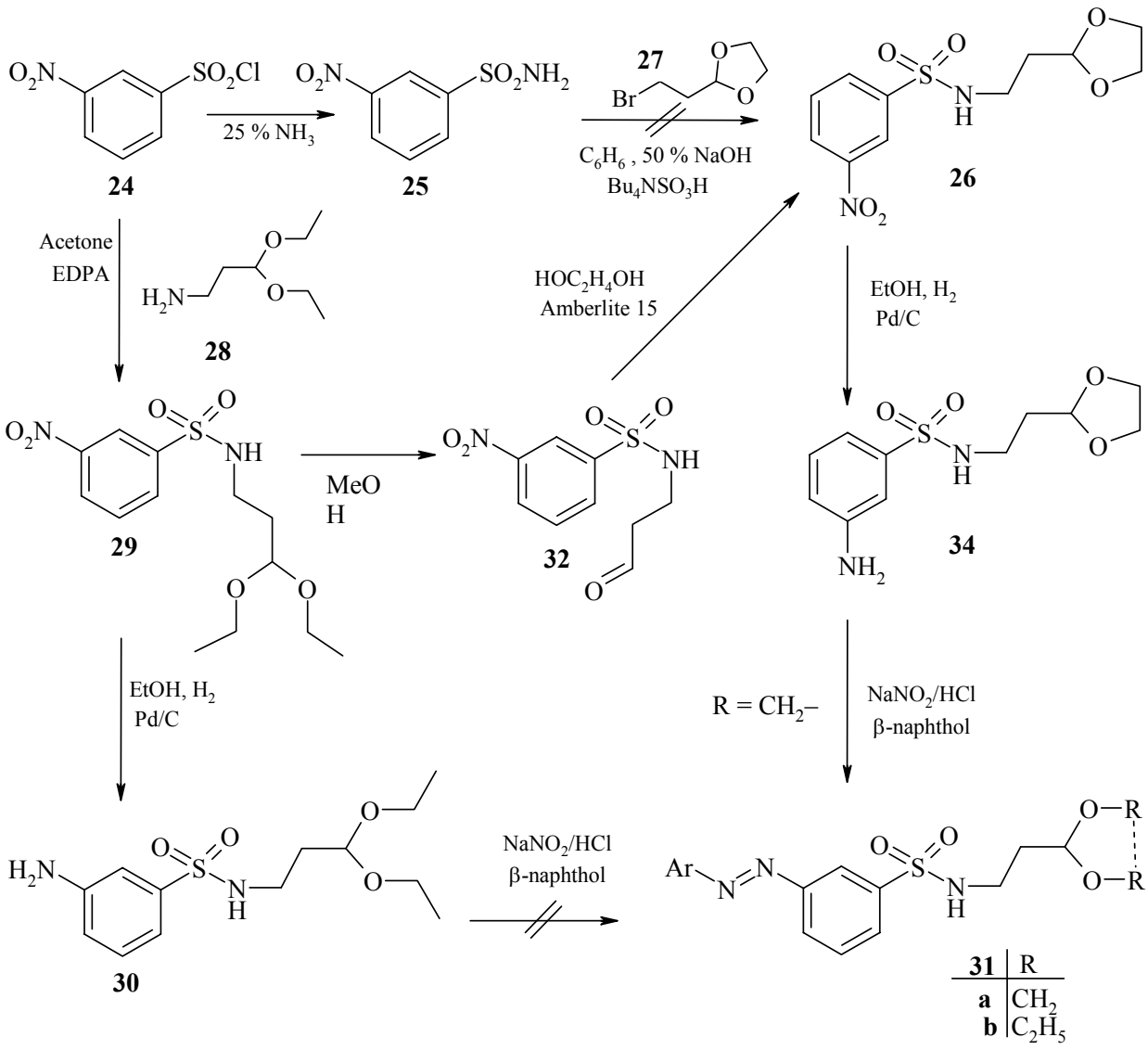


Fig 3–2: Structure of dye **21** in the crystal

The X–ray analysis of compound **21** shows that the dye prefer the ketohydrazono–form, confirming our hypothesis. As can be seen, there is an intramolecular hydrogen bond, where the proton is covalently bonded to the nitrogen atom. As mentioned above, in azo compounds the resonance stabilisation energy is a crucial factor. The loss of aromatic structure in the naphthol nucleus is compensated by the lower energy state of the iminone–form.

3.1.3. Synthesis of a diazo component with sulphonamide spacer

Besides alkylsulphones as the link between azo dye and reactive aldehyde group the use of a sulphonamide was investigated.



Scheme 3–7: Synthetic strategy for preparation of sulphonamido azo dyes

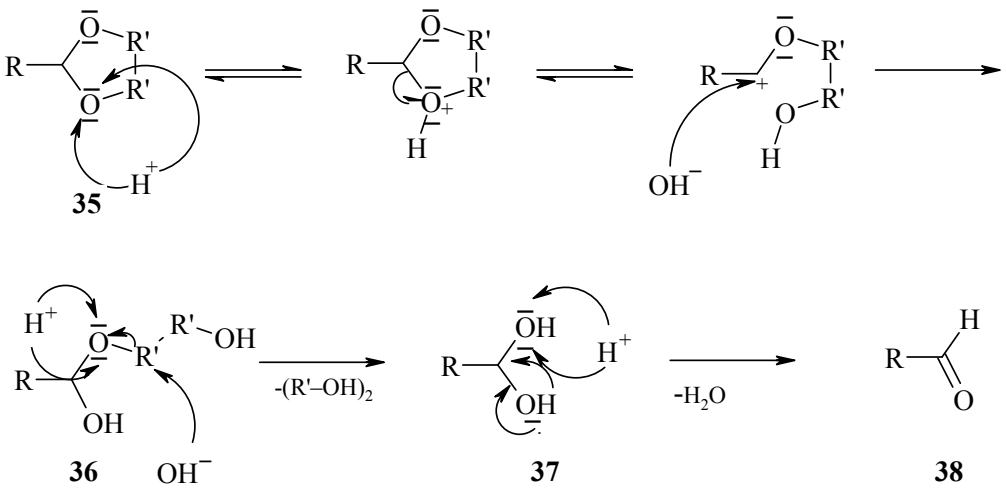
The synthetic strategy rests on the nucleophilic substitution of 3–nitrobenzenesulphonyl chloride **24** followed by the catalytic reduction with hydrogen, diazotisation and azo–coupling of the formed diazo component. On the other hand changes in the acceptor part of the azo–dye could affect the indicator properties of such H indicator dyes.

3.1.3.1. Preparation of nitroarylsulphonamidacetal 26

The synthesis of intermediate **25** was performed according to the procedure of Ludvig *et al*.[67] The sulphonyl chloride **24** was dissolved in dry acetone and added dropwise to a large excess of concentrated ammonia. The attempt to obtain compound **26** under heterogeneous conditions with tetrabutylamoniumhydrogensulphate as phase–transfer catalyst according to Gajda[68] failed, probably because of the very low nucleophilicity of the reagent **25**. In this case the nitro–group in *m*–position of the phenyl ring increases the NH–proton acidity and makes the substitution with 2–(2–bromoethyl)–[1,3] dioxolane **27** very difficult; therefore the yields were in the order of traces.

Another synthetic route, including the use of an acyclic acetal, was developed for the preparation of the sulphonamide spacer. Sulphonamide **29** was obtained as described in reference.[67] The choice of conditions was crucial to obtain high yields. The use of dry acetone supported good solubility of the reagents, as well as of the product and prevented the hydrolysis of sulphonyl chloride **24**. The temperature was controlled between 30 and 40 °C avoiding the double substitution by the aminoacetal **28**. Ethylendiisopropylamine (EDPA) was selected as base, it reacted with the HCl, evolved during the reaction. That helped to avoid the use of excess (> 2:1) **28**, as well as destroying the diethoxy group by the acid. After reaction, purification by FC afforded **29** in 87 % yield. The attempted distillation *in vacuo* was not successful, because of the decomposition of the substance at approximately 120 °C.

As is shown in Scheme 3–7 the preparation of azo–dye **31b**, bearing an acyclic acetal group was unsuccessful. Obviously, such acetals are quite unstable even at low temperatures under the influence of aqueous acidic solutions. The explanation could be that the cyclic acetals are accessible only of at outside of the ring for attack by protons, whereas acyclic ones can reach of both sides of the chain (Scheme 3–8). It is known that six membered rings are usually the most stable, but in the case of 1,3–dioxolanes five-numbered rings are more difficult to destroy than 6–membered ones (1,3–dioxanes).[69] It is probably due to the size of the cavity, the bigger ring allowing, in some conformations, the inside–attack of hydrogen ions.



Scheme 3–8: Deprotection of the acetals **35** under the influence of acid catalysts

The reaction shown in Scheme 3–8 passes through hemi–acetal **36**, which is rapidly hydrolysed to the hydrated form of the aldehyde **37**. Then a molecule of water is liberated under the influence of a proton and the aldehyde **38** is formed.

For the synthesis of more stable cyclic acetal another method was developed. Compound **29** was obtained according to a known procedure.[70, 71] Subsequently compound **32** was obtained through FC and then recrystallised from $CHCl_3$.

The introduction of the cyclic acetal–protective group was described by A. Dann *et al*.[72] and performed according to this procedure. The ion–exchange resin Amberlyst 15 acting as a catalyst formed an activated complex with the aldehyde and the reaction with ethylenglycole proceeded smoothly without taking off the water. The acetal **26** was extracted with ether and purified by FC in good yield (68 %), comparable with the reported in the literature (50-70 %).[72]

3.1.3.2. Reduction of nitroarylsulphonamide to the aniline–derivative 34

The reduction of the nitroacetal was performed using two methods: hydrogenation according to Janda *et al.*[73] and with $NaBH_4$ according to Neilson *et al.*[74] In both cases 10 % palladium over activated carbon was used as the catalyst.

The advantage of the first method is the simplicity of the procedure and the work–up. The main problems are undesired reactions between intermediates as hydroxylamine and nitroso compounds on one hand, and the aniline on the other. When the reaction time was extended

the acetal seemed to be opened and polar compounds were produced. Similar low stabilities of the cyclic acetals have been reported.[75] An additional disadvantage was the fact that the yields of the reaction were not reproducible.

The reduction with $NaBH_4$ has several advantages. The final reaction conditions are basic, preventing condensation between the intermediates, furthermore the reaction can be carried out in aqueous solutions. The desired acetal **34** was obtained after FC in very good yields (80 %).

3.1.4. Synthesis of reactive aldehyde pH–indicator azo dyes

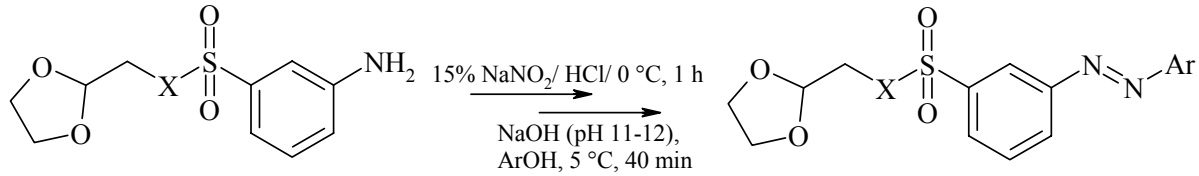
The acetal group can be reviewed as a double–ether linkage. It is known that this group is quite stable under alkaline conditions.[76] In order to incorporate this novel reactive group in the pH–indicator azo dyes, a synthetic method for preparation of aldehyde functionalised azo dyes was developed. The syntheses were realised as follows:

* First the dyes were prepared, bearing the [1,3]-dioxolan-2-yl group by azo–coupling reaction of a dioxolanyl sulphondiazonium salt with various hydroxyaryl compounds in alkaline conditions.

* In the second step the protection was removed in the presence of catalytic amounts of diluted inorganic acids and the reactive aldehydic azo dyes were successfully immobilised on the PVA *co*–polymer by the acetal linkage.

3.1.4.1. Preparation of azo dyes bearing a protective formyl group

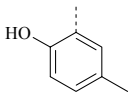
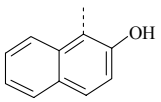
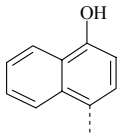
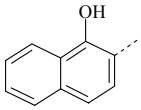
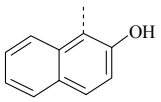
As mentioned in section 3.1.1.1 the synthesis of an azo dye by diazotisation from appropriate anilines followed by coupling with nucleophilic components, is the most important method for its preparation.



Scheme 3–9: Preparation of acetal–functionalised azo dyes **18**, **39**, **40**, **41** and **31a** (X = CH_2 or CH_2NH)

The results of the azo–coupling with the diazo components (Scheme 3–9) are shown in Table 3-1:

Table 3–1: Yields of azo–coupling reaction with 3–[2–([1,3]Dixolan–2–yl) ethanesulfonyl] aniline **23** and 3–Amino–*N*–(2–[1,3]dioxolan-2–yl–ethyl) benzenesulfonamide **34** with various aromatic substrates

Dye	Ar	X	Yield/ %
18		CH_2	80
39		CH_2	80
40		CH_2	70
41		CH_2	9.5
31a		CH_2NH	70

The protected aldehyde group in the diazo component is stable under the diazotisation conditions and the yields were reproducible (Table 3–1). One explanation of the stability of the functionalised azo dyes is the 5–membered ring, because it is known that cyclic acetals are much more stable compared with acyclic ones. Another reason is the low reaction temperature. However, small amounts of tars and very polar coloured compounds were produced as side products; these could not be avoided.

3.1.4.2. NMR spectra of acetal containing pH–indicator dyes

The ^1H NMR spectra of the acetals show a specific triplet (Fig. 3–3) for the methine proton H'. It appears in the region around 4.9 ppm with a coupling constant of 4–5 Hz. An exception

has been observed for intermediate **30**, where the signal is shifted upfield to ca. 4.50 ppm. Another characteristic signal is the multiplet around 3.9–5 ppm for the two–methylene units from the ethylenglycole residue. They show a typical AA'BB' pattern splitting of the bands, which is caused by their stereo-chemical difference.

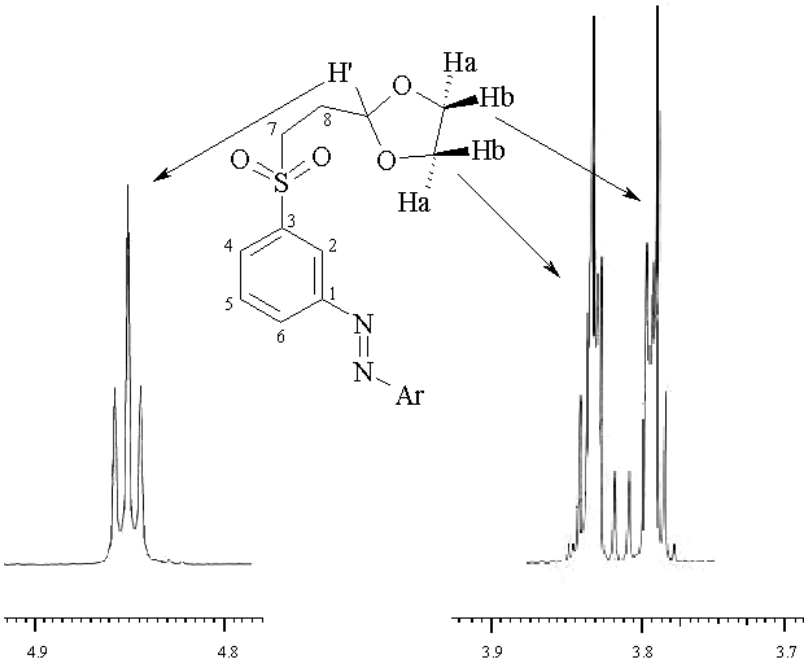


Figure 3–3: ^{1}H NMR spectral data of the acetal group in azo dyes **18**, **39**, **40**, **41** and **31a**

Both protons of the CH_2–group are situated under (Ha) and over (Hb) the plane defined by the [1,3]–dioxolane ring. This influence is caused from the steric hindrance of the sulphone group. The methylene unit, which is closer to that strong acceptor, is shifted to higher frequencies. The methylene protons at C-7 and C-8 positions do not appear as triplet and quartet, respectively. The signals of methylen protons neighbouring the sulphone group are also diastereofonic. There is an additional doublet split into triplet, caused from both hydrogen atoms in the C-8.

The aromatic protons in the acceptor part of the dye show the typical arrangement. The proton at C-2 gives a doublet around 8.30 ppm with a small *m*–coupling constant from 1.8 Hz with both protons at C-4 and C-6. The signal of proton at C-5 is a triplet around 7.6 ppm with an *o*–coupling constants of 7.8–8.1 Hz. Bothprotons at C-4 and C-6 show a very interesting doublet from doublet from doublets (ddd). It is due to the coupling with all other protons in the aromatic nuclei – one *o*– with C-5 proton and two *m*–couplings - with the protons at C-2 and between each other with the smallest *J* constant of 1.0 Hz. These phenomena are

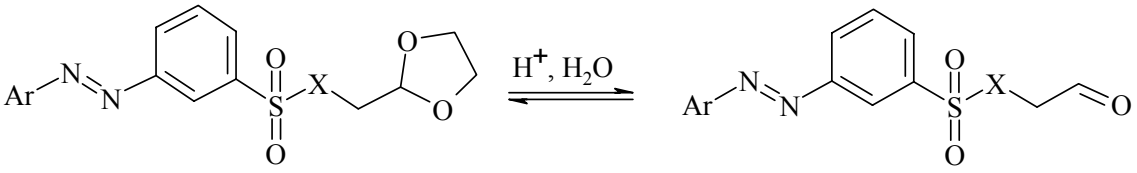
observed only for the *p*–cresol dye and intermediates. In all naphthol derivatives the fine interaction of these protons is lost, the bands are broaden.

The ^{13}C NMR spectra give also characteristic signals. The acetal carbon appears around 101 ppm. Both methylene carbons of the acetal ring are equivalent by that method and give a signal around 65 ppm.

These characteristic signals in the NMR spectra of acetal containing azo dyes are very important. Their availability allows to prove the covalent linkage of the reactive azo dyes to the poly(vinyl alcohol) backbone.

3.1.4.3. Cleavage of the protective group

The conversion of the cyclic acetals to the corresponding aldehydes were performed in acetone solution with diluted (15 %) sulphuric acid according to Gaony[77] (Scheme 3–10).



Scheme 3–10: Deprotection of the formyl groups of the dyes **19**, **44**, **45**, **46** and **47** (X = CH_2 or CH_2NH)

The reaction was carried out under reflux and reached its equilibrium after one hour. The problem here was the neutralisation with solid Na_2CO_3, as described in the literature.[77] However, this resulted in tar formation and produced very polar dyes. It was probably due to aldol condensation in the alkaline medium, because both methylene units between the sulphone/sulphonamide and carbonyl groups are very active. Aldehydes **19**, **44**, **45**, **46** and **47** were obtained in moderate good yields (68–80 %).

The compounds show a typical signal for the aldehyde functionality in the NMR spectra. In the ^1H NMR spectra it is observed around δ=9.6 ppm as a singlet, and only for the sulphonamide dye **47** it shows a coupling to the neighbouring methylene group and splits into a triplet with ^3J = 1.3 Hz. After deuterium exchange with D_2O these signals disappear. The hydrogen atoms in the methylene units between the carbonyl group and the arylsulphone are

registered as typical triplets with coupling constants of 7.0–7.8 Hz. This indicates, that the *n*–propanal chain has symmetry to the rest of the dye molecule.

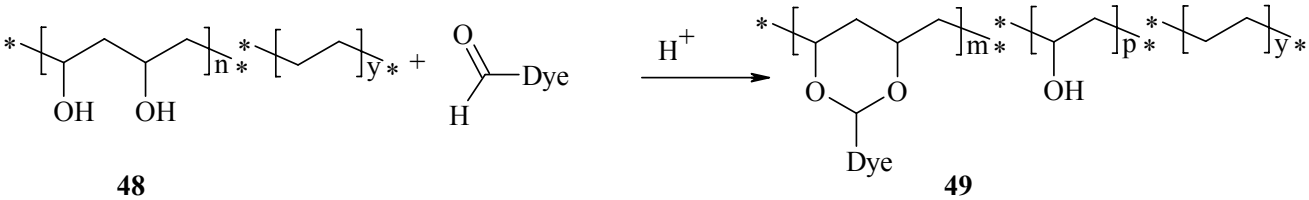
In the ^{13}C NMR spectra the carbonyl carbon atoms are observed around 193÷196 ppm, and the dye **47** gives a signal at 201.7 ppm.

The IR spectra of aldehyde group containing dyes show a typical Fermi doublet for the CH strech with overtones of the C–H bending mode at 2830 - 2850 and 2710 - 2730 cm^{-1} with low intensity. The characteristic signal of the C=O bond of the carbonyl group appears as a very strong band around 1720–1730 cm^{-1}.

3.1.4.4. Covalent connection of reactive dyes to poly(vinyl alcohol) units

The following methods are commonly used for producing poly(vinyl acetals): conversion of poly(vinyl acetate) into poly(vinyl alcohol) (PVA) in acidic solution followed by acetalisation,[78] and reaction of an aqueous solution of poly(vinyl alcohol) with an aldehyde and subsequent precipitation of the acetals.[79]

The presence of water in the acetalisation of PVA has no influence on the process, in contrast when the reagent are alcohols, where the driving force of the reaction is the removal of water from the reaction mixture.[80] The aim was to prepare pH-sensors with long-term stability within a wide range of alkaline pH. The sensors were based on azo dyes, which are covalently bond to a polymer matrix. On the other hand, PVAs are water–soluble, which is avoided by high–acetalised rubbers. These acetal membranes are not transparent, when they are exposed to aqueous surrounding. To be employed as sensors, the polymers have to fulfil the following conditions: they must be insoluble in water, they should show transparency in aqueous medium and be soluble in organic solvents. Therefore we decided to use PVA *co*–polymers, in particular poly(vinyl alcohol *co*–ethylene) polymers **48** (PVA *co*–PE), purchased from Aldrich, the structure of which is given in Scheme 3–11:



48 **49**

Scheme 3–11: Covalent binding of an aldehyde functionalised reactive azo dye with poly(vinyl alcohol *co*–ethylen) composites **49**

In order to form the acetal bond between dye and polymer there are required at least two adjacent vinyl alcohol units. In this case the connection unit consists of one six membered 1,3–dioxane ring, which gives additional stability of the dye–polymer composite. For this purpose a *co*-polymer with n ≥ y is required, *i.e.* its ethylene content must be at least half of the amount of the vinyl alcohol contribution.

The results are shown in Table 3–2:

Table 3–2: Details of dye–polymer covalent connection reactions

dye–polymer	dye connected	reaction time/h	percent connected/mol %
50	**19**	2.0	2.5
51	**44**	3.5	3.5
52	**45**	2.0	1.5
53	**46**	4.5	0.8
54	**47**	2.5	5.0

The amount of dyes, covalently linked to the polymers was estimated by the method of a calibration curve, based on UV/vis measurements.

3.1.4.5. Properties of dye–polymer composites

The covalent linkage of the dyes to the polymers by an acetal group was not found in the literature. The obtained sensitive materials have the following properties:

- No leaching or bleaching of the dye–polymer composites after standing for 6 months in 2 *N* NaOH solution was observed.
- Very thin membranes (app. 60 μm) were obtained after dissolution of the dye–polymer composites in DMF and subsequent evaporation of the solvent to dryness. They possessed good flexibility and transparency both with and without exposure to the alkaline solutions.
- The resulting sensor membranes exhibit a very short response–time (in the range of seconds) on changing the pH. This is due to the high polarity of the PVA–units in the polymer.

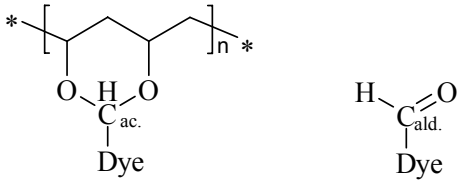
Therefore these conjugates can be applied for the preparation of sensitive layers in extrinsic fibre-optical sensors. The devices can be used for measurements at highly alkaline pHs during long periods of time without suffering of the signal.

3.1.4.6. Evidence for an acetal linkage to the poly(vinyl alcohol) units

All reactive azo dyes (**19**, **44**, **45**, **46**, and **47)** were successfully bound to the poly(vinyl alcohol) backbone by the acetal linkage. The progress of the reaction was monitored by thin layer chromtography (acetone or EtOAc as eluents) – the dye–polymer spot stayed on the start and the free dyes moved with the front. Different spectroscopic methods (*vide infra*) were employed to establish the nature of the linkage.

3.1.4.6.1. NMR–analysis of dye–polymer composites

As the most important analytical method to prove the acetal linkage, NMR spectra were employed, using a typical triplet around 4.8 to 5.0 ppm in the ^{1}H NMR spectrum for the acetal proton.



Scheme 3–12: Schematic representation of the acetal and aldehyde parts of the dyes

The aldehydic protons give signals between 9 and 10 ppm, usually a singlet (Scheme 3-12). In the ^{13}C NMR spectra another characteristic evidence can be found – the acetal carbon atom absorbs around 100 ppm, while the aldehyde carbon is registered at 200 ppm. In regard of the small percent of dyes in the dye–polymer conjugates (Table 3–2) the polymer bands overlap those of the dyes at all and expansion of the aromatic region was required.

The characteristic signals of the dye–polymer (PVA *co*–PE) conjugates in the ^{1}H NMR spectra are shown in expanded form in the region from 4.8 to 11 ppm, where the polymer has no resonance signal. ^{13}C NMR spectroscopy has not been employed in this case.

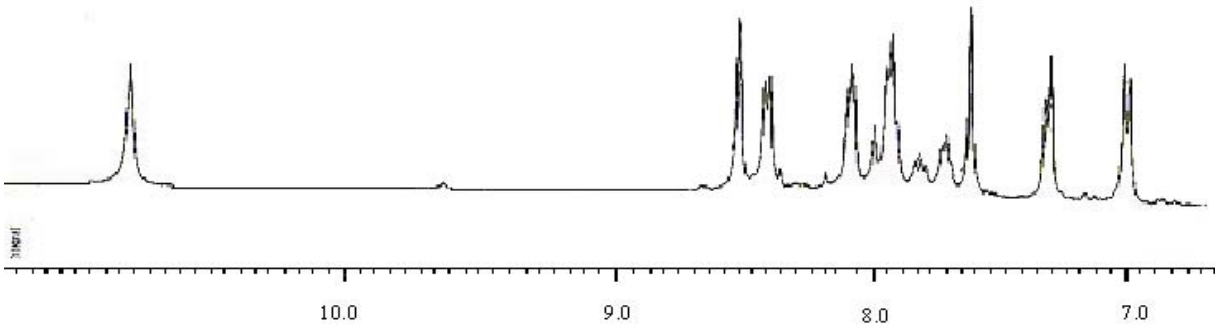


Figure 3–4: ^{1}H NMR spectrum of **50** (expansion of the region between 6.8 and 11 ppm)

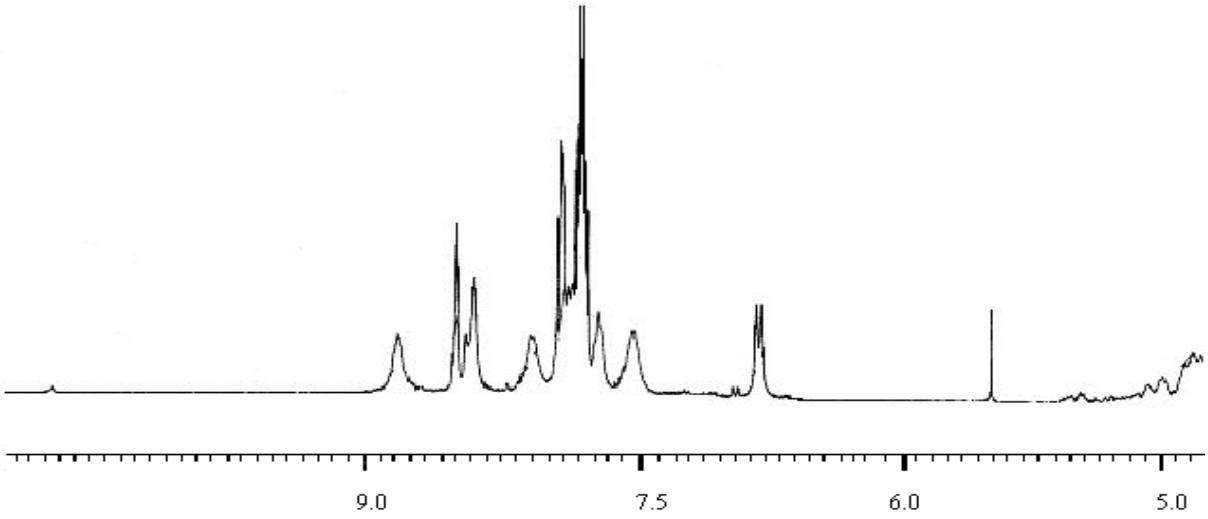


Figure 3–5: ^{1}H NMR spectrum of **51** (expansion of the region between 4.8 and 10 ppm)

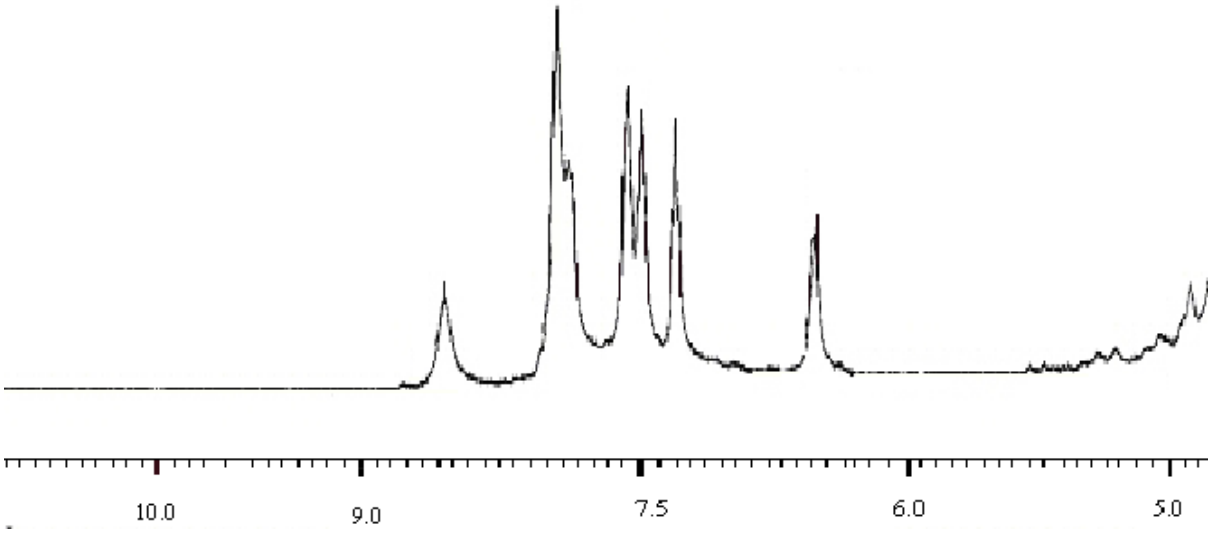


Figure 3–6: ^{1}H NMR spectrum of **52** (expansion of the region between 4.8 and 11 ppm)

There are no signals for aldehydic protons between 9 and 10 ppm (see Figures 3–4, 5, 6). Only very small shoulders are displayed around 9.55 (Fig. 3–5) and 10.2 (Fig. 3–6), which could belong to the remaining minimal amounts of unconnected dyes. The acetal protons can not be definitely determined, because of the influence of the polymer. Even in this case though, there are bands in the 4.8–5.0 ppm region, which could belong to the acetal connection. Typical for the polymer spectra is the fact that all signals are broad because of the chemical non–uniformity of the mixture.

Better results were obtained from acetal-bound dye **47** with pure PVA–dye–polymer **55**. In this case the aim was to bind as much as possible of dye to the poly(vinyl alcohol) backbone and to receive a high dye–content in the conjugate to obtain clear analytical evidence for those linkage. The ^{1}H NMR (199.982 MHz) and ^{13}C NMR (50.285 MHz) spectra are reproduced in the next two figures:

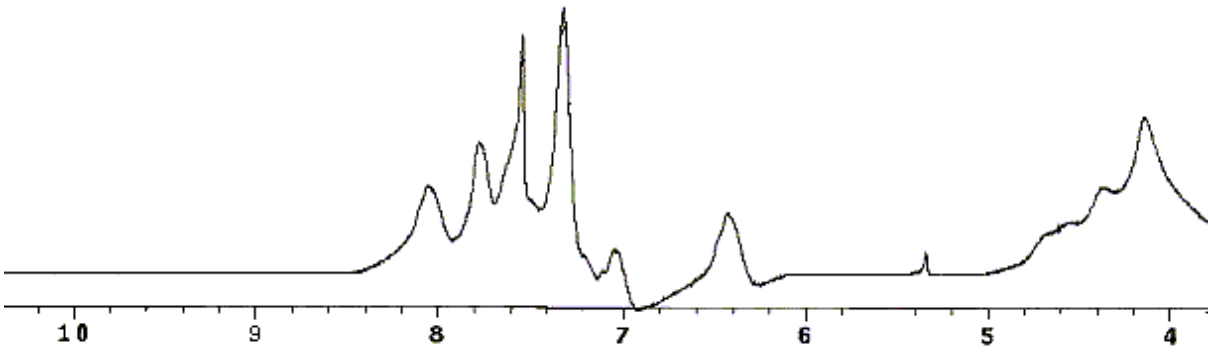


Figure 3–7: Section of the ^{1}H NMR spectrum of **55** between 3.9 and 10 ppm

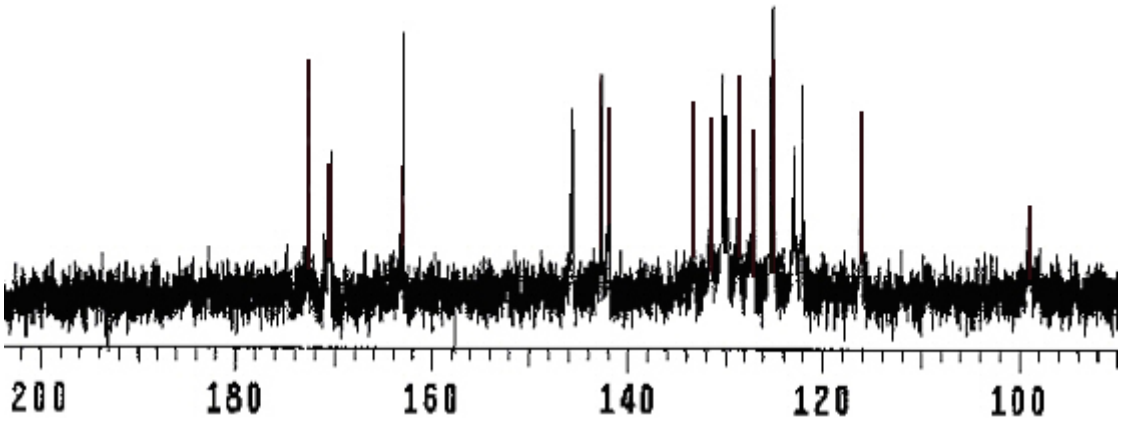


Figure 3–8: Section of the ^{13}C NMR spectrum of **55** between 90 and 200 ppm

There are not observed any aldehyde signals in the proton spectra between 9 and 11 ppm. Also, as for the other dye–polymer composites, it was impossible to identify the signal for the acetal proton exactly. On the other hand, in the ^{13}C NMR spectrum of conjugate **55**, as in the carbon spectra of acetal free dyes, a signal at 99.5 is clearly visible - the region, where the acetal–carbon atom usually appears. No absorption bands between 190 and 205 ppm for carbonyl carbon atoms were observed.

In summary, the NMR–spectra give good evidence for the acetal linkage of the dyes to the polyvinyl backbone. The dyes do not possess typical signals for the aldehyde functionality, but the polymer absorption disturbs the determination of the triplet of the acetal–proton. ^{13}C NMR spectroscopy plays no role for PVA *co*–PE–composites, but this method gives important information about the binding of the dyes for PVA of conjugate **55**.

3.1.4.6.2. IR–analysis of the dye–polymer composites

IR-spectroscopy was another analytical method to confirm the covalent binding of the dyes to the polymer backbone. Typical bands for the carbonyl group should appear in the region between 1700 and 1730 cm^{-1}. This absorption band is particulary valuable, since it possesses a high intensity and can hence be identified even in small concentrations. From another viewpoint the possible influence of the polymer as a medium to influence the tautomeric equilibrium of the azo dyes must be concidered. The hydrazone form also has a carbonyl function.

The signals for the acetal function appear between 1130 and 1280 cm^{-1}, where the C–O–C ether group absorbs. It was difficult to identify these bands, because of overlap with other bands.

Sections of the IR–spectra of PVA *co*–PE **48** and poly(vinyl butyral) (PVB) (Aldrich) are shown in Figure 3–9 and those of dye–polymer composites **52** and **53** are given in Figure 3–10.

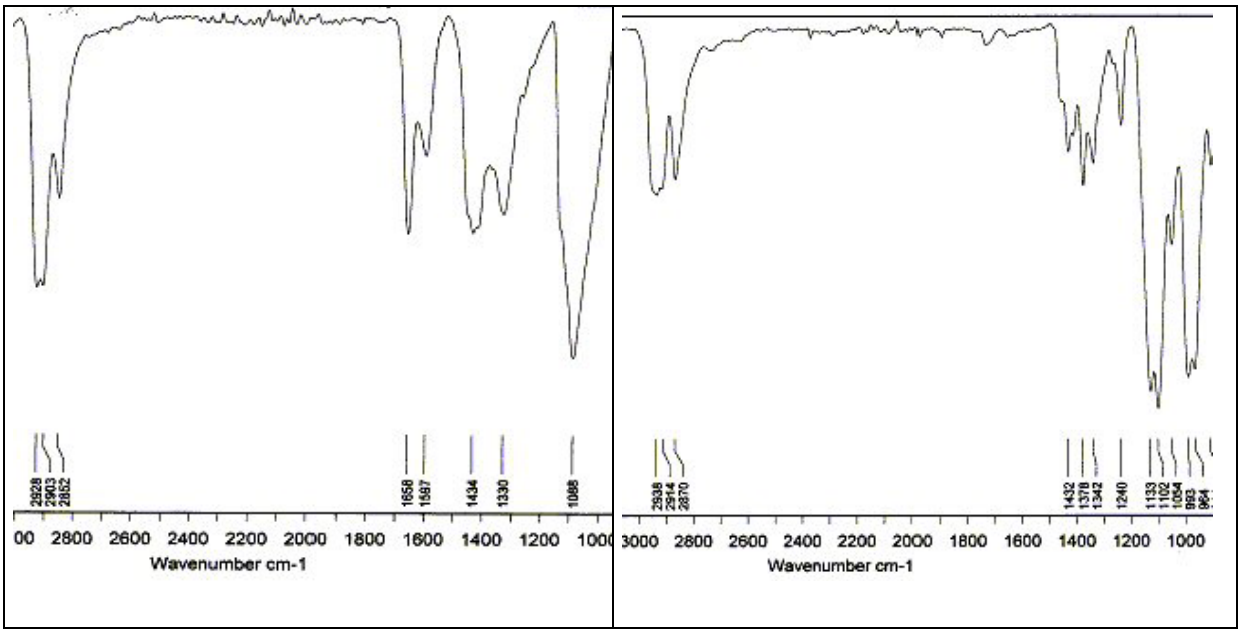


Figure 3–9: Section (1000–3000 cm^{-1}) of the IR–spectra of **48** (left) and PVB (right)

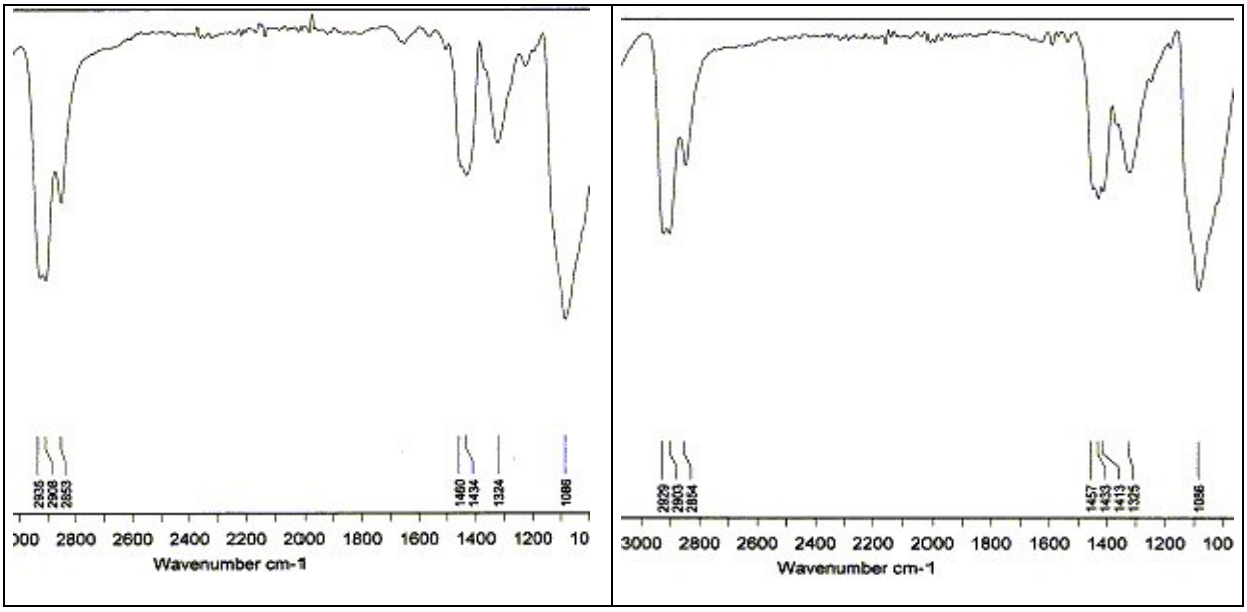


Figure 3–10: Section (1000–3000 cm^{-1}) of IR–spectra for conjugates **53** (left) and **52** (right)

The PVA *co* PE possesses typical aliphatic C–H streching bands (CH_2 and CH) from 2860 to 2930 cm^{-1} and the absorption at 1430 cm^{-1} is due to CH_2-scissor vibrations and CH_3 antisymmetric deformations. The band at 1658 cm^{-1} is typical for PVA and can be assigned to the C=C stretching mode of the monomer. The bands at 1330 and 1068 cm^{-1} belong to C–O stretching and O–H deformation vibrations. PVB has almost the same CH bands, but at lower

wavenumber two very strong bands at 1102 and 1133 cm^{-1} were registered, typical C-O-C stretching bands for cyclic ethers.

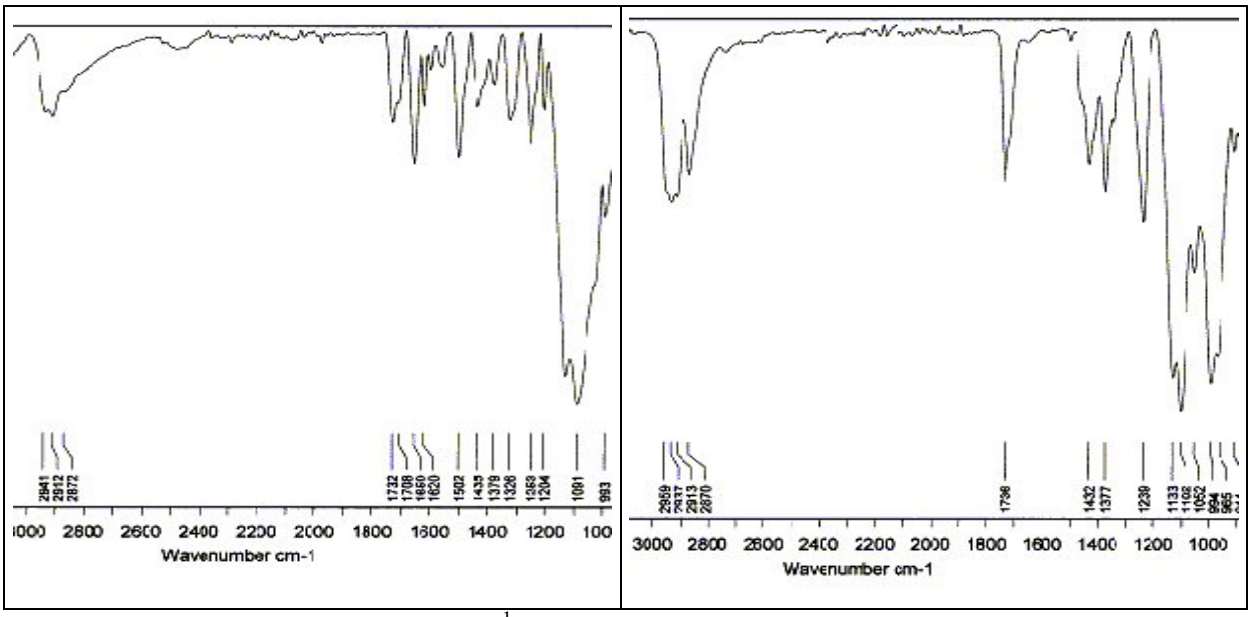


Figure 3–11: Section (1000–3000 cm^{-1}) of IR–spectra for conjugates **55** (left) and **56** (right)

No absorptions in the carbonyl group range are observed. Very small bands between 1200–1300 cm^{-1} and the signals around 1100 cm^{-1} can not be assigned to the acetal functionality because of the influence of a strong absorption at 1086 cm^{-1}. However, it can be seen, that dye–polymer composites **52** and **53** do not possess a carbonyl group. The dyes bound to the polymer exist in their hydroxyazo tautomer forms (see section 3.3.1.1.1.). Obviously, the hydrophobic part of the **48** gives relative unpolarity to the *co*-polymer and favours the tautomeric form.

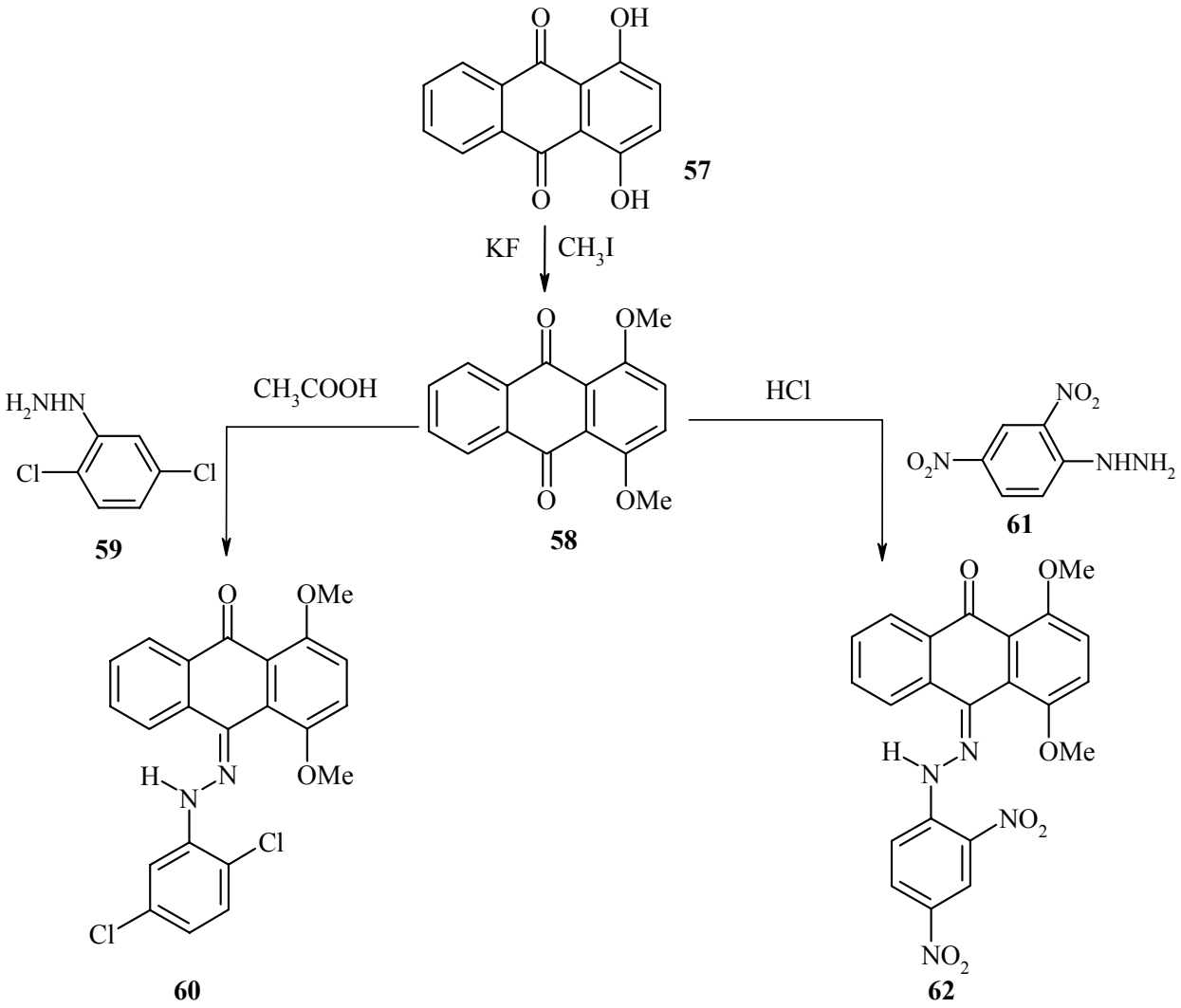
Different tautomeric forms were observed in conjugates **55** and **56**, which were prepared with more polar PVA. The more polar environment causes a shift of the equilibrium and the dyes, bound to the polymer, exist predominantly in their hydrazone form. The bands at 1732 and 1708 cm^{-1} correspond to the C=O and C=N stretching motion of the ketohydrazone–tautomer of the dye, which are typical for 6–membered cyclic unsaturated ketones. The absorptions are shifted to higher frequency around 15-25 cm^{-1} from the signals for the aldehyde bands of the dye–precursor. The signals of the acetal functionality can be recognised – small band at 1253 cm^{-1} and stronger absorption around 1100 cm^{-1} which is due to the high dye concentration in the composite.

Similar behaviour can be observed in the spectrum of composite **56** - there is a band at 1736 cm^{-1}, which belongs to the hydrazono form. The signals in the range from 1100 to

1240 cm^{-1} are typical for the acetal–containing polymer and are almost the same as those for purchased material from Aldrich PVB (Fig. 3–9).
The IR–spectra gave additional proof of the acetal linkage of the aldehyde–containing dyes bound to the PVA chain.

3.1.5. Synthesis of anthraquinone monophenylhydrazone dyes by condensation reaction

The synthesised phenol and naphthol azo dyes and the corresponding dye–polymer composites cover the pH–region from 9 to 12.5. In order to extend the sensors capability up to pH=14 anthraquinonemonophenylhydrazone dyes **60** and **62** were developed. In this case the dyes were completed by condensation reactions of phenylhydrazine derivatives with 1,4-dimethoxyanthraquinone **58** (see Scheme 3–13). It is known that these kinds of azo dyes exist in the ketohydrazone form completelly because of a high resonance stabilisation energy.[81] As expected, their colour changes are realised at higher pH.
No exact procedure of the condensation with anthraquinone was found in the literature, therefore the reaction of 1,4-naphthoquinone derivatives with phenylhydrazine derivatives was used. The synthesis of intermediate **58** was performed analogously to Boone *et al.*[82] from quinazarine **57**. The reaction was simplified by using KF as base, and DMF was used as a solvent instead of DMSO. The suspension was stirred for 10 h at 60 °C to yield di– and monosubstituted compounds. Whereas the colour of the reagent (quinazarine **57**) is red–orange, the monoether derivative has an orange colour and the dimethoxy compound **58** is yellow, corresponding to reduced delocalisation in the parent substance. **58** was prepared in moderate yields from 40 to 45 %. The condensation of 2,5–dichlorophenylhydrazine **59** with 1,4–naphthoquinone as been described by Kalmeyer and Kruppert,[83] and the preparation of dye **60** was carried out analogously in EtOH/HOAc medium.



Scheme 3–13: Synthesis of anthraquinone monophenylhydrazone dyes **60** and **62**

The reaction solution was refluxed for 4 h and stirred further 20 h at room temperature. As a result product **60** separated as crystals. The pure dye was obtained by FC and subsequently by recrystallisation from ethanol in 58 % yield.

For the synthesis of dye **62** a procedure given by Fryling *et al*[84] was used. In this case the higher acidity of the hydrazine group in 2,4–dinitrophenylhydrazine **61** required the use of hydrochloric acid instead of HOAc. The reaction was carried out under reflux conditions for 3 h and then stirred overnight at room temperature.

3.2. Synthesis of chloride–sensitive dyes

In order to monitor the corrosion attack in reinforced concrete it is necessary to develop sensitive dyes, whose changes in optical properties depend on the chloride ion concentration. These indicators require independence from high alkaline medium (pH~12.5) and in the presence of other ionic species like sulphate, carbonate and phosphate, which typically occurr in concrete constructions. Appropriate polymers are needed to complete the sensor material body. They have to be transparent at the measured wavelengths under realistic conditions. Both dyes and polymers should be stable for long periods of time under these extremely aggressive environments.

3.2.1. Synthesis of 9–(10–H) acridones and acridines

As mentioned in section **1.3.1.2**, for optical detection of chloride ions, fluorescence quenching of certain heteroaromatic substances was used.[32–34]
The most often utilised dyes for such determinations are quinoline–, 9–acridone– or acridine derivatives, where the aromatic nitrogen atom is substituted or quaternised. The main problem is that hydroxyl as well as chloride ions cause quenching of the fluorescence. Research in this field was based on the reported higher stability of 4–methoxy–9–acridone comparised with 9–acridone towards fluorescence quenching.[85]

3.2.1.1. Synthesis of 9–(10–H) acridones

The synthesis of 9–acridones was carried out in two principle stages (Fig. 3–12):
I. *N*-phenylanthranilic acid was prepared using an intramolecular cyclisation.

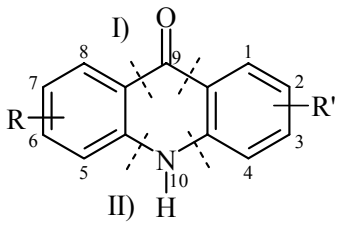
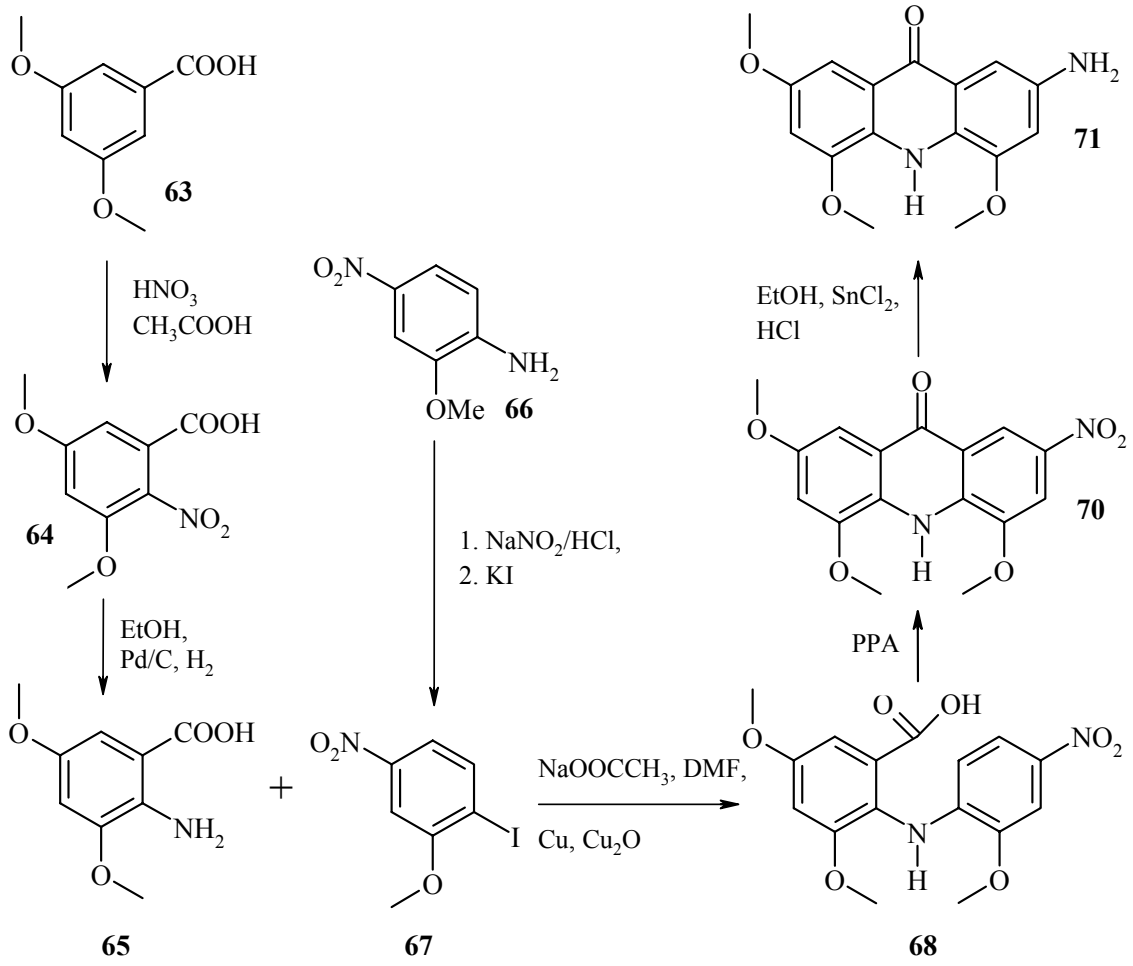


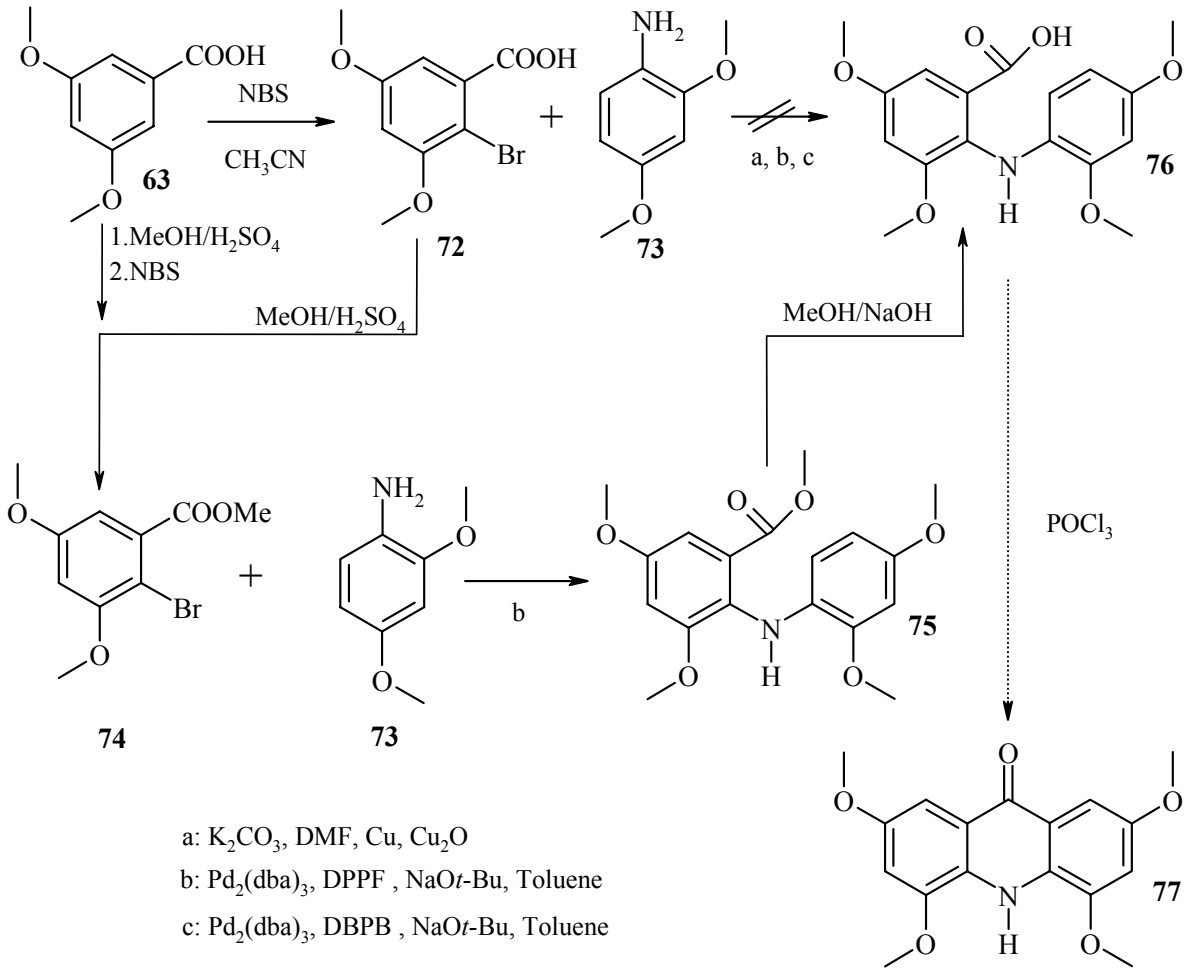
Figure 3–12: Principle stages in the synthesis of 9–acridone (R, R'–common substituents)

II. The heterocyclic compound was then produced according to the S_eAr–mechanism.
The dashed lines in Fig. 3-12 show the variability in the synthesis of these compounds. Both synthetic routes were used – *via* preparation of anthranilic acid derivatives (route A) and subsequent coupling with halogenophenyl compounds (Scheme 3–14) and by reaction of 2-halogenobenzoic acid (route B) with aniline derivatives (Scheme 3–15).



Scheme 3–14: Synthesis of 9–acridone derivatives through anthranilic acid (route A)

In route A a substituent, which is suitable for nucleophilic substitution was used, because the electron density is decreased, due to the electron withdrawing effect of the nitro–group. This functionality was converted later to an amino group, planned to play a spacer role in the polymer.



Scheme 3–15: Synthesis of 9–acridone derivatives *via* 2–halogenobenzoic acids (route B)

Route B (*via* 2–halogenobenzoic acid) was chosen for the synthesis of tetramethoxy derivatives. Here, both phenyl nuclei bear electron–donating substituents and the carboxylic group is the only one which gives assistance to the new C–N bond formation-process with its negative inductive and mesomeric effects.

The catalytic reduction of compound **64** was performed in a Parr apparatus with 10 % Pd over carbon as the catalyst in ethanol. In this case anthranilic acid **65** was obtained in 91 % yield, higher than by chemical reduction with $FeSO_4$ and NH_3, which is given in the literature as 69 %.[92] The simple work–up in this kind of reduction is of additional advantage.

3.2.1.1.1. Synthesis of *o*–substituted 3,5–dimethoxybenzoic acid 72

As expected electrophilic substitution of 3,5–dimethoxybenzoic acid **63** takes place in C-2 utilising the *o*-/*p*-directing effct of the methoxy group. Both nitration and bromination reactions were performed under mild conditions to avoid the formation of undesired by–products.

The nitration reaction was carried out according to Insole.[86] Intermediate **64** was recrystallised from ethanol and used without further purification.

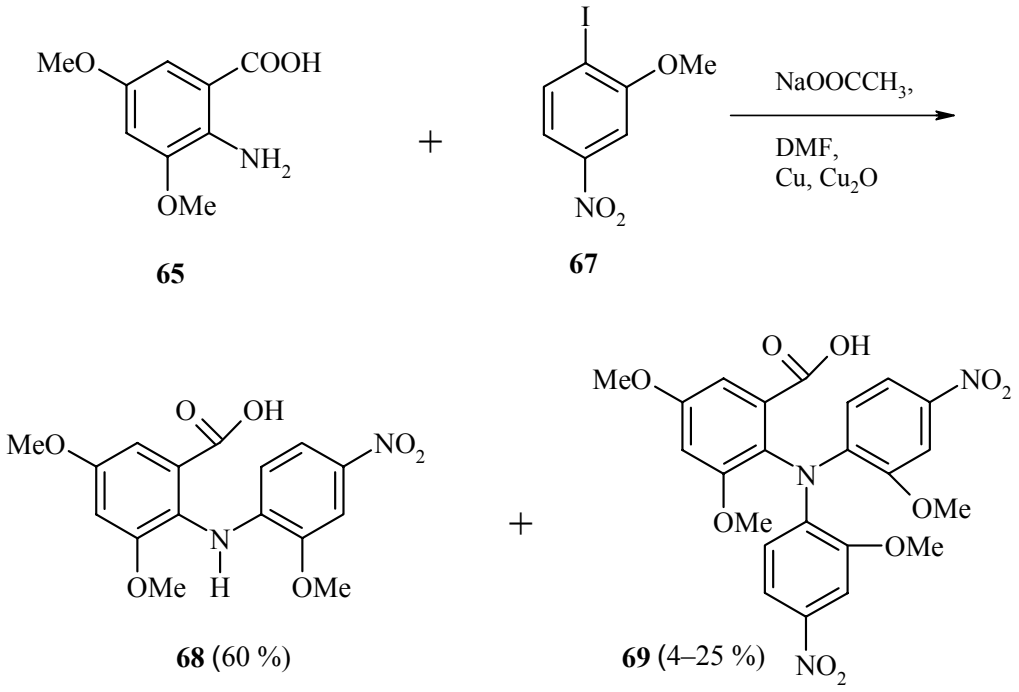
The choice of acetic acid as solvent was very important. When sulphuric acid was used, tar formation was observed with many side–products, and the temperature control was more difficult.

Bromination of these activated aromatic substrates with NBS is well know.[87–89] The *o*–bromobenzoic acid derivative **72** was obtained after Kugelrohr distillation under reduced pressure as a pale oil, which slowly solidified to white prisms.

3.2.1.1.2. Synthesis of *N*–arylanthranilic acid derivatives 68, 75 and 76

The synthesis of polymethoxy 9–acridones has been described by Brockmann *et al.*[90] Dimethoxyanthranilic acid was coupled with different halogenopolymethoxybenzenes by Ullmann–coupling. Compound **67** was prepared as halogenated–agent. The iodine atom is the easiest for substitution by different nucleophiles. In this case the additional activity is enhanced by the *p*-nitro–group. The synthesis was performed by Sandmeyer substitution from aniline–derivative **66** according to Hanford and Adams[91] in quantitative yield (96 %). Due to the very good solubility of the produced diazonium salt the reaction was very easy to monitor. The Sandmeyer substitution was then carried out with the excess of KI. Product **67** was purified (more than 96 %, ^{1}H NMR-analyses) by simple recrystallisation from ethanol.

Ullmann couplingn for the synthesis of *N*–phenylanthranilic acid derivative **68** gave best results when DMF was used as solvent with catalytic amounts of Cu–powder and Cu_2O. Anhydrous sodium acetate was employed as base instead of K_2CO_3, because the undesired double substitution at the nitrogen atom took place yielding compound **69** for in significant amounts. However, this side reaction could not be avoided totally, and in the final mixture traces of the starting material **65**, product **68** and by–product **69** were always found (Scheme 3–16):



Scheme 3–16: Ullmann coupling of anthranilic acid derivatives

Triphenylamino–derivative **69** shows a weak fluorescence and its spot on TLC appeared near the spot of the desired product **68** in different solvent mixtures. It was removed after FC and recrystallisation from methanol. Substance **68** was obtained as yellow needles, which became darker on standing, with yields up to 60 %.

The attempts to synthese *N*–phenylanthranilic acid derivative **75** by Ullmann coupling gave the desired compound only in traces with many by-products, which could not be separated. Different reaction conditions were tried: varying the solvent, copper (I) salt, use of different bases, the results were always poor. The experiment with methylanthranilate **74** gave a slightly better result, but it was not satisfactory for synthetic purposes.

In this case route B was employed. The synthesised ester derivative **74** was employed in the Pd–catalysed C–N coupling reaction. Recently Miyaura has published a monograph about these cross coupling reactions.[93] Palladium-catalysed C–N bond formation uses a variety of catalysts–systems. Different $Pd^{(0)}$ and Pd^{2+} were applied[94–96] and numerous compounds have been used as a ligands in the reaction.[95–98] As base NaO*t*-Bu is usually applied,[94–98] only in a few cases Cs_2CO_3 is preferred as a milder reagent.[99]

Direct synthesis of compound **76** from 2–bromobenzoic acid derivative **72** was unsuccessful. Probably the carboxyl anion formed with the base blocked the catalyst. With methyl ester **74**

the reaction was carried out for 12 hours in dry toluene and product **75** was obtained in 22 % yield.

For the synthesis of compound **75** a catalyst system of $Pd^{(0)}_2(dba)_3$ (1.5 mol %) and diphosphorophenylferocene (DPPF) (2.2 mol %) as the ligand was used. The other synthetic routes were performed using $Pd^{(0)}_2(dba)_3$ with 2-(di-*t*-butylphosphino) biphenyl (DBPB) and Pd $(Ac)_2$ with DPPF or DBPB as catalytic systems, but the yields could not be improved (usually between 10 and 15 %). NaO*t*-Bu was used as a base in equimolar quantity with regard to the aniline–compound **73** and in 1.4–fold excess compared with the halogeno–substance.

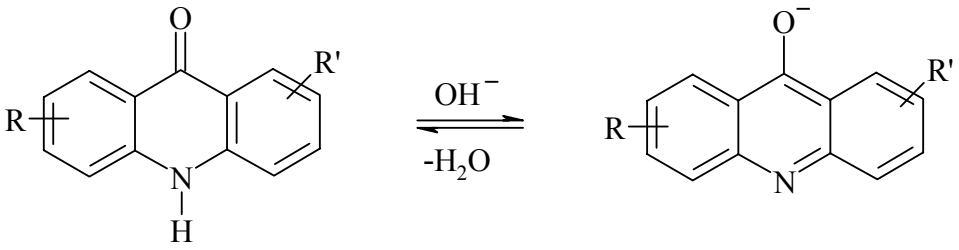
The cleavage of the ester group was carried out as usual in methanol with aqueous alkali. After recrystallisation from ethanol the product **76** was isolated as brightly yellow plates.

3.2.1.1.3. Synthesis of 9–acridone derivatives 70, 71 and 77

The intramolecular cyclisation of *N*–phenylanthranilic acid derivatives to 9–acridones can be performed with different cyclisation agents – conc. H_2SO_4,[100] $POCl_3$ or PCl_5[101] or poly phosphoric acid (PPA).[102] Brockmann *et al.* have described the synthesis of methoxy–acridones using PPA.[90] The advantages of this method are weak oxidation capability compared to conc. H_2SO_4, an absence of demethylation and side products like 9–chloroacridines formed when $POCl_3$ or PCl_5 are employed. PPA has one disadvantage - it has a very high viscosity up to 60 °C, which makes the handling with the compound difficult. At high temperatures this problem can be overcome. Acridone **70** was obtained in 60 % yield after recrystallisation from ethanol/DMF as deep orange needles, which became darker on standing. Its methanolic solution has a weak yellow fluorescence, which disappeared on long standing in air.

To improve the fluorescence properties and to prepare a group, capable of acting as a spacer to the polymers, the nitro group was converted into amino group. The reduction was performed with $SnCl_2$ and 10 *N* HCl according to Goldberg and Kelly.[103] Aminoacridone **71** yielded orange needles, whose ethanolic solution shows a strong yellow–orange fluorescence. The solution is very sensitive to air and in a short time the colour became darker and after hours it changed to brown. In order to prevent the oxidation, compound **71** was converted to its hydrochloride. In this form it was possible to obtain ^{1}H NMR and MS spectra, but other analyses failed.

These measurements have shown that at high pH (12–14) the fluorescence of methoxy acridone was not quenched, moreover it became even stronger and the emission maxima changed. This phenomenon could be due to the tautomerism of these compounds and further deprotonation of the hydroxyl group:



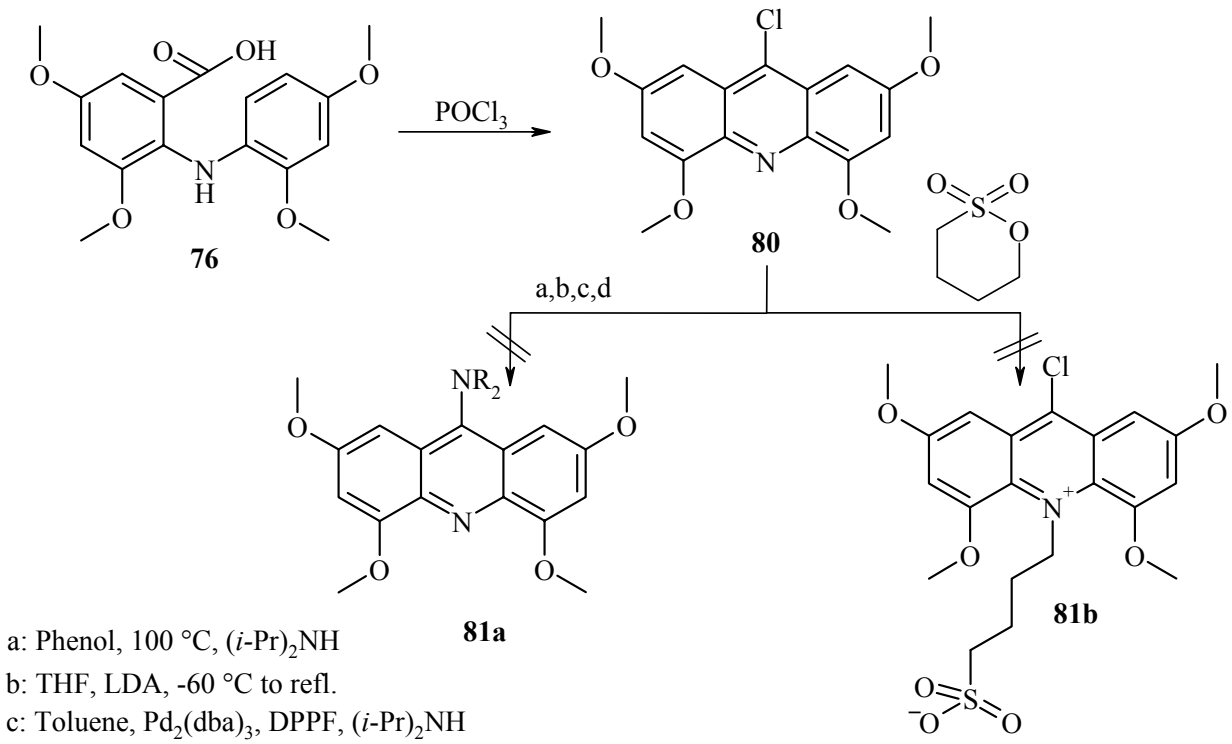
78 **79**

Figure 3–13: Fluorescence of 9–acridones in highly alkaline medium

The 9–hydroxyacridinium anion **79** possesses a very stable fluorescence, because of the easier excitation of the electron–rich species as proposed by Kokubun[104] and Wolfbeis and Huber[105].

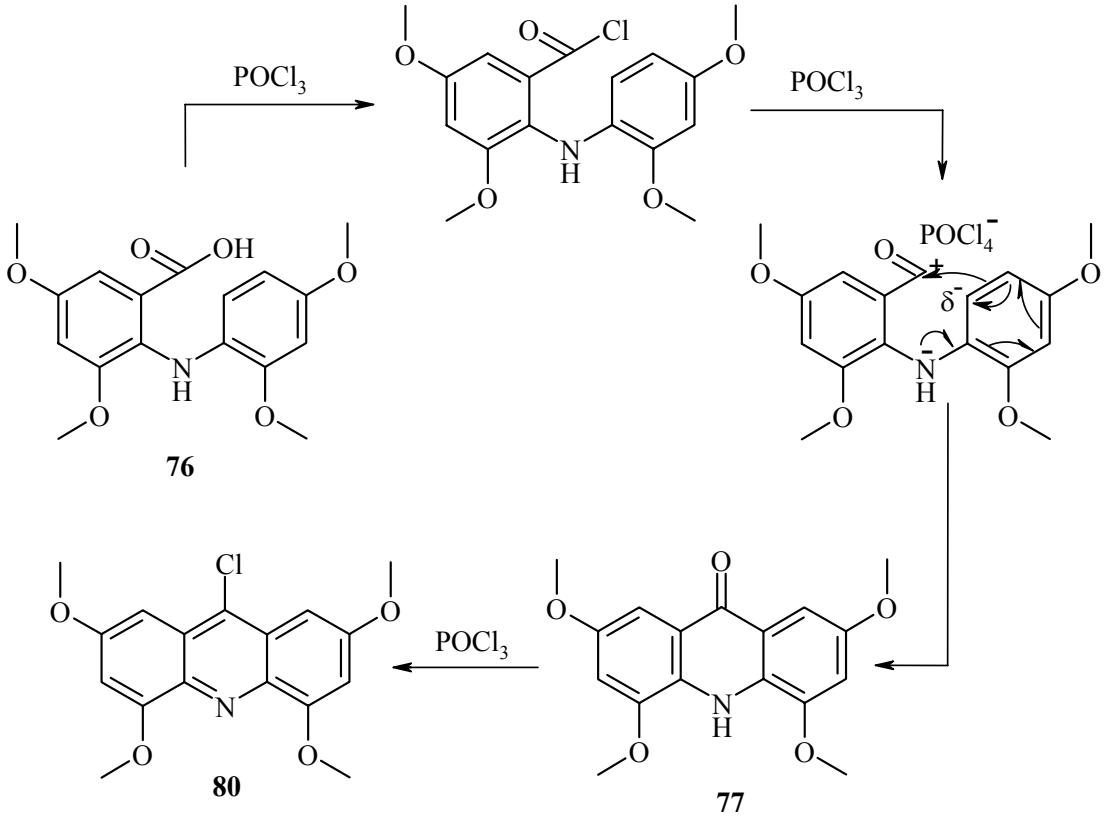
3.2.1.1.4. Synthesis of acridines 81

The next goal was to synthesise the tetramethoxyacridines **80** etc., which have to be dialkylamino–substituted at the C-9 position and quaternised with 1,4–butansultone **97b**:



Scheme 3–17: Attempts to synthesis of tetramethoxyacridines **81a** and **81b**

The synthesis of 9–chloroacridine **80** was carried out analogously to Lehmstedt and Schrader.[106] The reaction sequence involved four steps:



Scheme 3–18: Intermediates in the synthesis of 9–chloroacridine **81** from **76** with $POCl_3$

First the acidic chloride is produced by the action of $POCl_3$. Then another molecule of phosphoryl chloride acts as Lewis acid and generates the activated carbocation in the second step. That cation is involved in an intramolecular electrophilic substitution (Friedel-Crafts acylation) and in the third step intermediate **77** is produced, which undergoes further halogenation with the phosphoryl chloride. Therefore, a large excess of $POCl_3$ is required. After work-up, product **80** was purified by recrystallisation from DMF/water to afford orange needles (yield 60 %). The demethylation was not observed in this case, probably due to the milder action of the $POCl_3$.

The conversion to 9–*N,N*–dialkylaminoacridine **81a** failed. The phenol–mediated method was tried[107, 108] with di–*i*–propylamine and di–*n*–butylamine, which resulted only in hydrolysed products and the 9–phenoxy intermediate. Further attempts were performed with LDA in dry THF, but compound **80** remained unchanged. In a last experiment Pd–catalysed coupling was performed as described above, but unfortunately also with negative results.

In the temeprature interval of 90–120 °C the quaternisation approach with 1,4–butanesultone did not give the desired product **81b**, probably of because of steric hinderance at the aromatic

nitrogen in the temprature interval 90–120 °C. When the temperature was increased to 140 °C tar formation occured.

3.2.2. Synthesis of trimethine dyes

The polymethine dyes can be regarded to be constructed of three different parts: two end groups, which are joined by a conjugated chain of methine carbon atoms. When both end groups are identical, the dyes are called symmetrical polymethines. When they are different we speak of unsymmetrical polymethines. In this study only symmetrical trimethine dyes will be examined, since it is known, that they have better aggregation properties.[38] Benzimidazolocarbotrimethines have two advantages – firstly, they delocalise the positive charge more efficiently between the four nitrogen atoms and in this way enhance the symmetry of the molecule. Secondly, the 5,6,5',6'–tetrahalogeno substituted benzimidazolotrimethines possess an additional symmetry element, an axis, passing the carbon atoms in the 2,2' positions.

3.2.2.1. Methods for synthesis of trimethine dyes

3.2.2.1.1. General aspects

The synthesis of trimethines can be divided into two main categories. In the first approach a trimethine chain is formed by coupling of suitable end groups (Fig. 3–14, b, c). Alternatively ring closure condensation reactions at one (Fig. 3–14, a) or both sides (Fig. 3–14, a, d) between *o*–amino phenols or thiophenols with ω– or α,ω–functionalised chain synthon–compounds can be performed. These reactions are carried out in the presence of acids and one equivalent of water or HX is released.

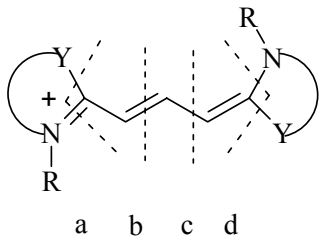
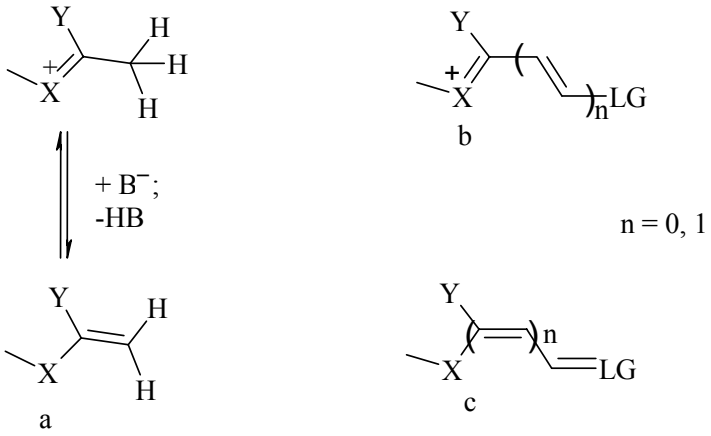


Figure 3–14: Different routes to trimethines (Y = NR, S, O and CR_2)

In the second approach *N*–alkylation/quaternisation is the subsequent step and a condensation or an oxidation reaction to complete the cyclic or acyclic methine chain follows it.[109]
There are two different end group synthons which are used in the synthesis of polymethines: an activated methylene or a methyl group, a CH–acid (Scheme 3–19, a), and a compound with a suitable leaving group (LG) such as a neutral molecule (Scheme 3–19, b) or an anion (Scheme 3–19, c).

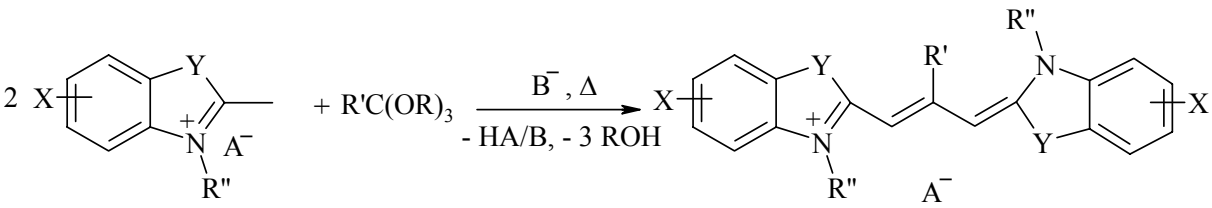


Scheme 3–19: Two types of end group synthons for the synthesis of trimethine dyes, where X = NR, O, S, Se etc; Y = NR_2, O, S, CR_3 *etc*; LG = OR, SR, NR_2, NR, O, S *etc*; B = base.

In the case of end groups with activated methyl functionality, the equilibrium is very often shifted, *in situ*, to the methylene synthon, which is actually the reacting nucleophile. Therefore, these compounds are called methylene bases. The process is influenced by the use of bases such as pyridine or alkoxides, where the proton is abstracted to form the reactive nucleophilic species.

3.2.2.1.2. Synthesis of trimethines *via* the orthoester–method

The orthoester method has been applicated only for the synthesis of symmetrical trimethines. The chemical process is described on the following scheme:



82 **83** **84**

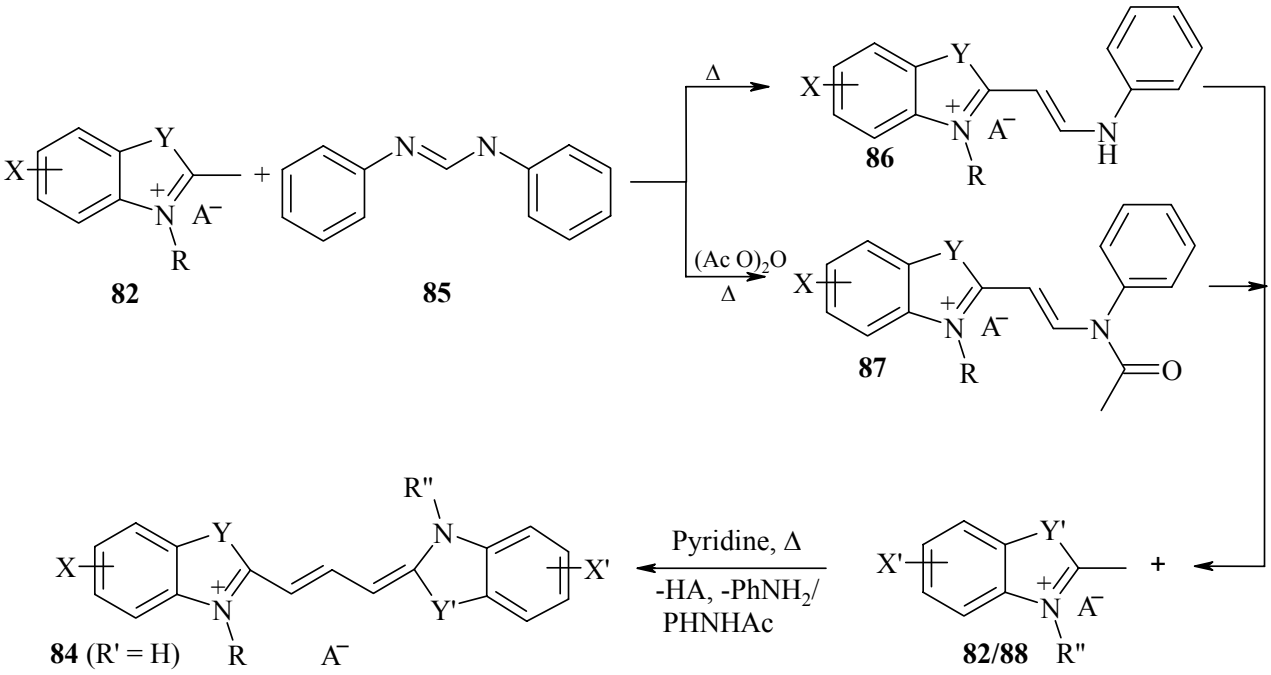
Scheme 3–20: Synthesis of trimethines by the orthoester method: X = common substituents; Y = NR, CR_2, O, S, Se etc; A^- = counter anion; R' = H or alkyl; R = alkyl; R" = alkyl or other carbon–chain functionality; B^- = base.

This synthetic method was discovered by Koenig[110] and is appropriate for many classes of quaternary salts with a variety of substituents in the aromatic ring. As base dry pyridine is usually used[111] and in some cases mixtures of pyridine and other organic–amino bases has been reported.[112]

In this work the orthoester–method was also applied, but the results were not satisfactory.

3.2.2.1.3. Synthesis of trimethines using the diphenylformamidine–method

The synthesis of trimethines by coupling of *N,N*–diphenylformamidine is a two–stage process, applicable for the preparation of symmetrical as well as unsymmetrical dyes:



Scheme 3–21: Synthesis of trimethine dyes by the phenylformamidine method: X, X' = common substituents; Y, Y' = NR, CR_2, O, S, Se etc; A^- = counter anion; R; R' = alkyl or other carbon–chain functionality

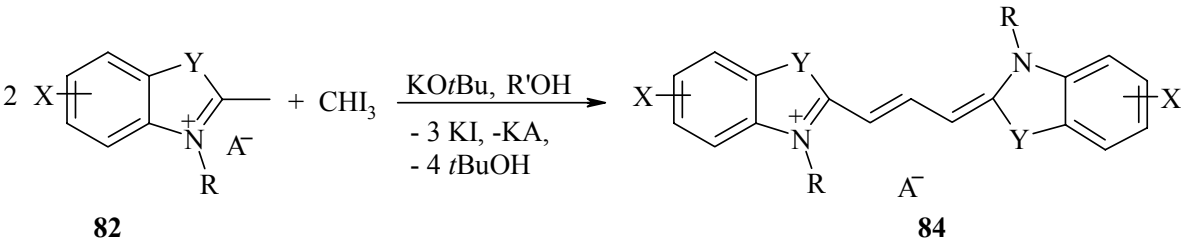
The first step can be carried out with or without activating agents (e.g. acetic anhydride[113]) for the subsequent nucleophilic attack, and yields the corresponding anilinovinyl **86** or anilidovinyl **87** compounds, often called ICI,[112–114] which usually can be isolated. When the condensation is performed without anhydride,[40a] the reactions are conducted in *n*–PrOH or DMSO at high temperatures (130–180 °C) for several hours while the solvents and the produced aniline are removed by distillation. When acetic anhydride is applied, the reaction is carried out at reflux for 30 – 60 min; the use of *p*–toluensulphonylchloride has also been reported as separate reaction.[114]

The second stage is carried out similary to the orthoester–method - *i.e.* upon action of pyridine the precursor ICI is coupled with another molecule of methylene base **82** or **88** on heating to form the trimethine dye.

In this study the phenylformamidine method was also employed, but the second step gave very poor results only.

3.2.2.1.4. Synthesis of trimethines according to De Rossi

The synthesis according to De Rossi *et al.*[40a] involves the use of potassium or sodium *t*–butoxides in dry alcohols. Iodoform is used as a coupling component, because the iodine atoms are very suitable for nucleophilic replacement:



82 **84**

Scheme 3–22: Synthesis of trimethine dyes according to De Rossi *et al.*[40a]: X = common substituents; Y = NR, CR_2, O, S, Se etc; A^- = counter anion; R' = methyl or ethyl; R = alkyl or other carbon–chain functionality

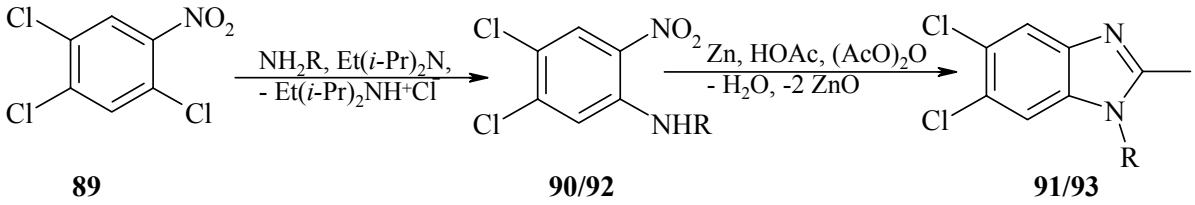
The reactions are performed under mild condition - *i.e.* from room temperature to 70 – 80 °C. At least a fourfold excess of alkoxide is required (Scheme 3–22), to allow for replacement of the counter ion. This synthetic method was the most often used in the present work and practically all benzimidazolocarbocyanines were obtained this manner. The yields were moderate to good (15 to 50 % - lit.[66]: 17–35 %), depending on their nature, betaine structure, and the often very difficult purification. The trimethine dyes are readily soluble in aqueous solutions and in some cases tend to build *J*–aggregates in hydrophobic organic solvents such as CH_2Cl_2 or toluene.

3.2.2.2. Synthesis of 5,6,5',6'–tetrahalogeno–trimethines

In this investigation two kinds of tetrahalogeno–substituted trimethines were synthesised: 5,6,5',6'–tetrachloro- and 5,6,5',6'–tetrabromo derivatives. The first type of dye was obtained by the synthetic scheme given in reference.[40a] For the tetrabromo–derivative **106** another preparative route was developed.

3.2.2.2.1. Synthesis of 1–alkyl–5,6–dichloro–2–methylbenzimidazoles

As mentioned above, the synthesis of dichlorobenzimidazoles was carried out according to De Rossi *et al.*[40a] The synthetic route is shown in following scheme:



89 **90/92** **91/93**

Scheme 3–23: Synthesis of intermediates **90** and **92** and benzimidazoles **91** and **93** according to De Rossi *et al.*[40a]: R = C_4H_9 or C_6H_{13}

The nucleophilic substitution of 2,4,5–trichloronitrobenzene **89** with *N*–alkylamines in *i*-PrOH, with Et(*i*-Pr)$_2$N (EDPA) as base first produces intermediates **90/92** in high yield for the first one (86 % vs 48 % reported in the Lit.[40a] for R = C_4H_9). Further reduction with Zn/HOAc gave functionalised *o*–phenylenedimanines, which are formed *in situ*, and subsequent intramolecular cyclisation with Ac_2O yielded benzimidazoles **91/93**.

3.2.2.2.1.1. Preparation of N–alkyl–4,5–dichloro–2–nitroanilines 90 and 92

The reaction is a *N*–arylation of alkylamines, which is facilitated by the electronegative nitro–group. Two of the three Cl–atoms are under the influence of negative M–effects, while the one in ortho–position received additional mobility from the negative I effect of the substituent. However, the reaction produced two by–products - 4– and 2,4–*N*–alkylated nitroanilines (TLC), these undesired compounds were easily removed from the mixture by recrystallisation, due to their low percentage.

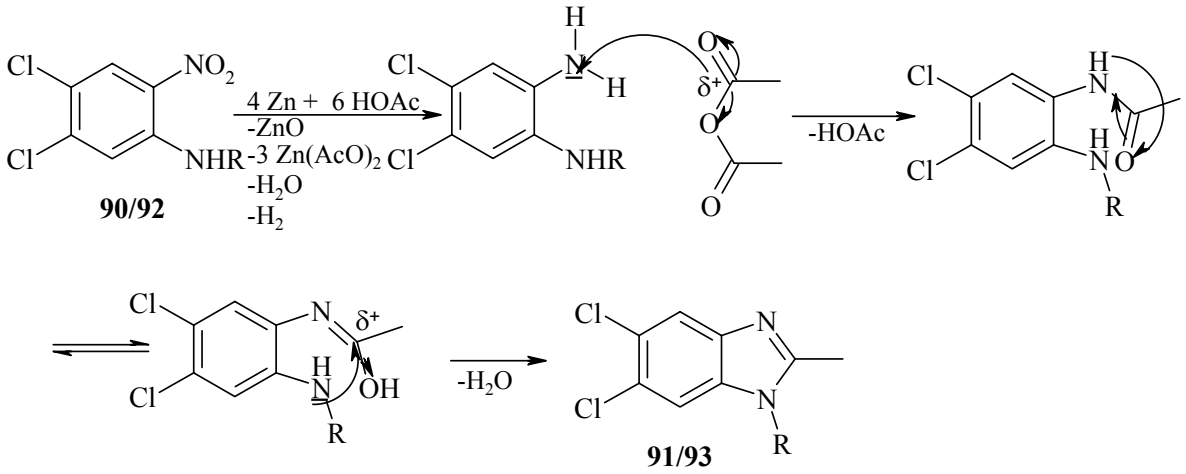
The nucleophilic substitution of the starting material **89** afforded compounds **90** and **92** by a superior procedure, as given in literature[40a] (Scheme 3–22). As solvent *i*–PrOH was chosen, it allows to apply higher temperatures and offers further advantages in the purification step. The EDPA was used to trap the liberated HCl, and in this way it was not necessary to use the alkylamine in great excess. Furthermore, the organic base can not be quaternised under these conditions, because of its bigger volume and steric hindrance. The reaction details and yields of the intermediates **90** and **92** are given in Table 3–3:

Table 3–3: Synthesis of *N*–alkyl–4,5–dichloro–2–nitroanilines

R	Compound	Reaction Time/h	Yield/ % theor.	m. p./ °C	ref.[No] Yield/% ;	m. p./°C
C_4H_9	**90**	8	86	66–67	48[40 a]	62–63[40 a]
C_6H_{13}	**92**	16	77	43	–	–

3.2.2.2.1.2. Preparation of dichlorobenzimidazoles 91 and 93

The reduction and intramolecular cyclisation of *N*–alkyl–dichloro–*o*–nitroanilines was carried out in one step (Scheme 3–23). *In situ* generated compounds **90** and **92** were transformed to the corresponding *o*–phenylendiamine derivatives with Zn/HOAc in 1,2–dichloroethane. The proposed mechanism of the reaction is given in the next scheme:



Scheme 3–24: Proposed mechanism for the reductive cyclisation of **90**/**92** to **91**/**93**

5,6–Dichlorobenzimidazoles **91** and **93** were obtained as white needles in moderate to good yields after recrystallisation from unpolar solvent mixtures. The details are given in Table 3–4:

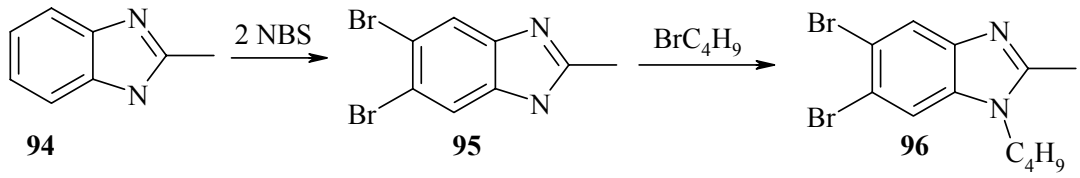
Table 3–4: Synthesis of *N*–alkyl–5,6–dichloro–2–methylbenzimidazoles **91/93**

R	Compound	Reaction time/h	Yield/% theor	m. p./ °C	Solvent for recryst.	ref.[No] Yield/% ;	m. p./°C
C_4H_9	**91**	16	83.7	114	EtOAc/ *n*–hexane	88[40 a]	106–108[40 a]
C_6H_{13}	**93**	24	58	119	*n*–hexane	–	–

3.2.2.2.2. Synthesis of 1–butyl–5,6–dibromo–2–methylbenzimidazole 96

The synthesis of the tetrabromotrimethine dyes was performed in order to prove the better *J*–aggregation properties of derivatives with a bulky substituent in the aromatic part of the end groups.

1–Butyl–5,6–dibromo–2–methylbenzimidazole **96** was prepared using the route from 2–methylbenzimidazole **94** (Scheme 3–25), because the bromo–atoms are easier to substitute, while amination of 2,4,5–tribromonitrobenzene would probably give large amounts of by–products.



Scheme 3–25: Preparation of the dibromo–benzimidazole derivative **96**[115, 116]

First the dibromo–derivative **95** was prepared and then *N*–alkylated to prevent possible tautomerism of the N–H–proton and to activate both 5– and 6–position of the benzimidazole for electrophilic substitution.

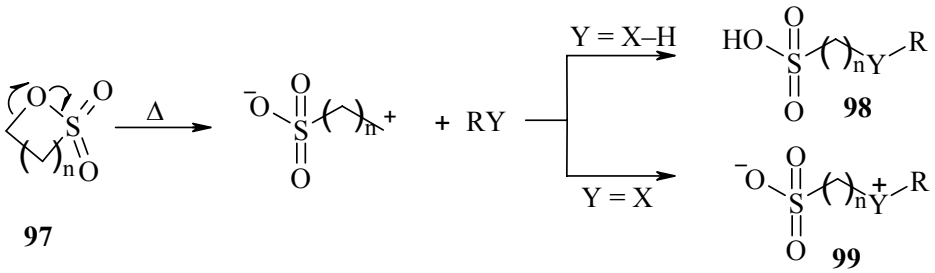
NBS was preferred as bromination agent as it is easier to handle and not so dangerous as bromine, as reported by Kihel *et al.*[115] Other disadvantages of the liquid reagent are formation of hydrobromide salts during the deactivation of the molecule for the second substitution, and formation of tars, which were observed when repeating the original procedure. Acetic acid was used as solvent.[115] The pure compound **95** was obtained as light–yellow prisms in 52 % yield.

The *N*–alkylation was performed by an improved procedure following Kyride *et al.*[116], in which instead of 50 % NaOH, anhydrous K_2CO_3 was used as the base in 1.3–fold excess. *i*-PrOH was chosen as solvent, in regard of the good solubility of compound **95**. These reactions are difficult for benzimidazoles because the NH–group possesses low nucleophilicity. The hydrogen atom is rather acidic, making stronger bases necessary. The use of NaH[117] and solid KOH[118] have been reported, since they deprotonate the NH function completely converting the benzimidazolium anion a more effective nucleophile. The desired compound **96** was obtained in 78 % yield after 6 h of reflux. The alkylated substance was extracted with EtOAc and purified by FC and appeared as white needles.

3.2.2.2.3. Synthesis of benzimidazolobetaines through quaternisation with 1,4-butanesultone 97b

The quaternisation of 1–alkyl–5,6–dihalogeno–2–methylbenzimidazoles with 1,4-butansultone **97b** was carried out according to De Rossi *et al.* [40a]

α, ω–Butanesultones **97** are cyclic internal ester of α–hydroxyalkyl–ω–sulfonic acids and they are often used as powerful sulphoalkylating agents of heteroatoms such as N, O, S.[119–121] The proposed mechanism of alkylation is given in Scheme 3–26:



n = 1, 2, 3; Y = attacked functionality, X = N, O, S

Scheme 3–26: Mechanism of alkylation of heteroatoms with α,ω–alkylsultones **97**

1,3–Propansultone **97a** (n = 2) is often used because of its higher activity due to the stronger ring tension of the five membered ring. As a result a chain with one carbon atom less is produced with respect to butyl.

The reactions are carried out either without solvent or in solvents with a high boiling point such as toluene, xylene, or halogenated benzenes.[119] In this study chlorobenzene or *o*–

dichlorobenzene were used in order to achieve higher reaction temperatures. The reaction details are given in Table 3–5:

Table 3–5: Quaternisation of benzimidazoles with 1,4–butanesultone **97b** (see Scheme 3-27)

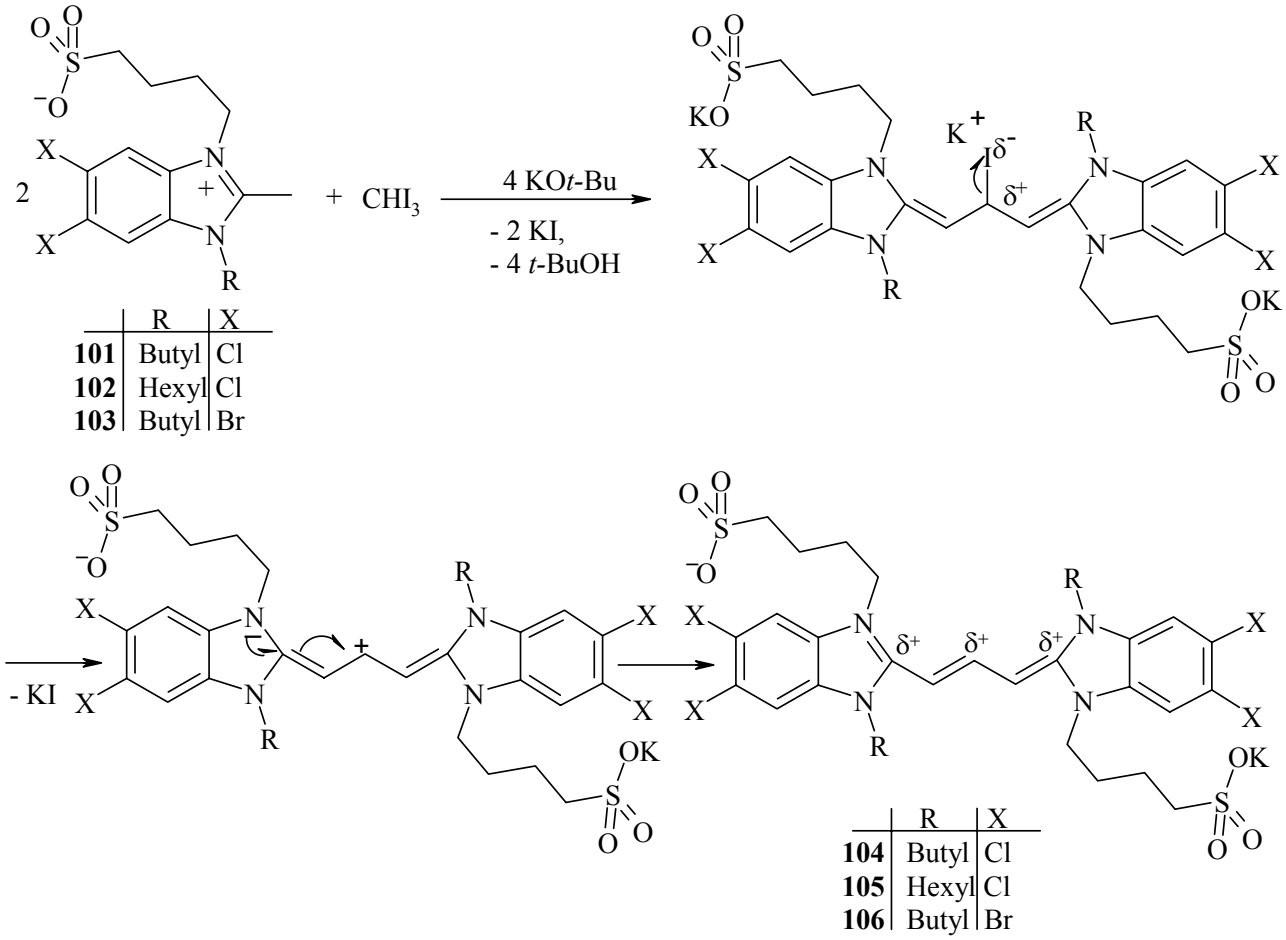
Compound	Hal.	N–alkyl	React. time, /h	Yield/ % theor	m. p., /°C	Solvent for recryst.
101	Cl	butyl	4	60	310–312	EtOH/ DMF
102	Cl	hexyl	9	74	301	EtOH*
103	Br	butyl	20	98	>320	EtOH/ H_2O

(*–boiling for 30 min)

Compound **103** shows the highest stability on standing under normal laboratory conditions. No decolourisation of the crystals was observed. 1–Hexyl–compound **102** was not completely dissolved in EtOH during the attempted recrystallisation, but in other solvents the deep pink–red colour of the solution appeared and made the yield worse. Methylene base **101** possesses poor solubility in organic solvents at room temperature, therefore the NMR–spectra were recorded in D_2O at 60 °C, where satisfactory concentrations for analysis were achieved.

3.2.2.2.4. Synthesis of benzimidazolotrimethines through coupling with CHI_3

The preparation of trimethines requires two equivalents of methylene base (Scheme 3–27), which react with iodoform in the presence of excess of alkaline alkoxides to form trimethine dyes. The strong base ensures the active form of the betaine even at room temperature for attack of positive centre of the haloform molecule. The choice of base and the concentration of tert–butoxide anion are also important. Under the applied conditions the undesired nucleophilic attack of the already prepared dye at the electron deficient carbon atoms of the methine chain is avoided.



	R	X
101	Butyl	Cl
102	Hexyl	Cl
103	Butyl	Br

	R	X
104	Butyl	Cl
105	Hexyl	Cl
106	Butyl	Br

Scheme 3–27: Mechanism of formation of trimethine dyes

The last step consists in the abstraction of the iodide anion and completion of the methine chain. Several final structures are possible: the betaine–potassium salt (Scheme 3–27); inner salt only (by protonation of the second sulphono acid function), while double potassium salt with counter anion for the whole molecule - *t*-BuO^- or OH^- depending on the method of purification. To obtain pure dyes by the described procedure *i.e.* dissolving them in DMSO and further precipitation with water[40a] and breaking (brown colour of the solution) of the chromophore chain or formation of *J*–aggregates upon influence of the aqueous environment was observed. The reaction details and purification methods are given in Table 3–6:

Table 3–6: Reaction and purification details for the synthesis of 5,6,5',6'–tetrahalogeno trimethines

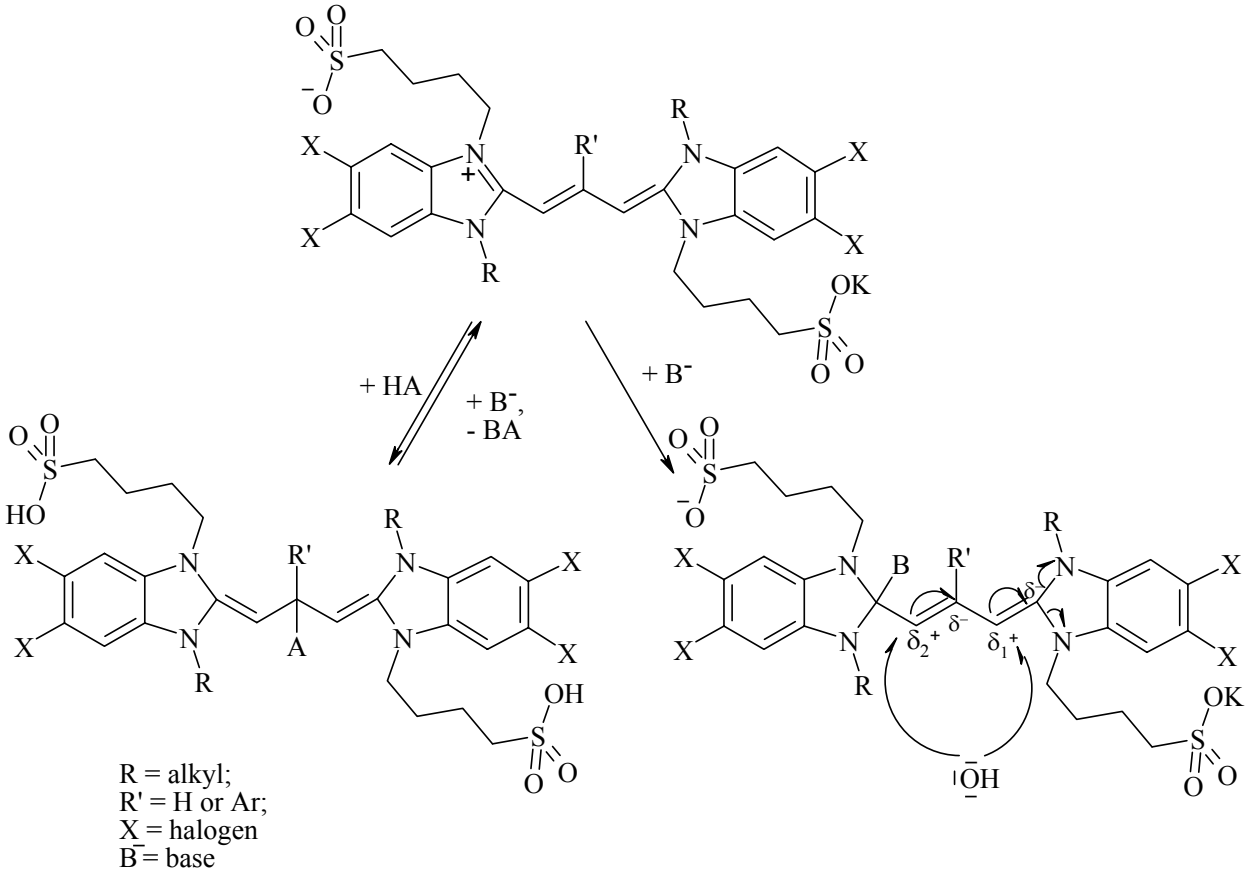
Comp	Hal.	N–alkyl	React. time, /h;/T/ C	React. solvent	Yield /% theor.	m. p., /°C	Purification
104	Cl	butyl	0.5, RT/ 5 min, 50	MeOH	48.0	273	2 × hot extr. (EtOH)
105	Cl	hexyl	1, RT/1, 60	MeOH	15.0	230–233	2 × hot extr. (MeOH)
106	Br	butyl	3, RT	EtOH	28.6	252–254	recryst. (DMF/ water)

Tetrabromo trimethine **106** was obtained by recrystallisation from DMF/water - deep violet needles after drying *in vacuo* at 50 °C. The crystals became dark–red on standing, probably due to the absorption of water from the air. Tetrachloro cyanines (**104** and **105**) afforded dark red crystals with strong yellow–green metallic lustre after twofold hot–extraction with EtOH and MeOH, which is typical for these dyes.

The nature of the synthesis (liberation of 3 equivalents of KI) together with the betaine ionic structure made the puriffication of the dyes difficult, resulting in low yields.

Polymethine dyes are physically and chemically rather labile. Aggressive environments, high temperatures *etc* lead to their destruction and loss of colour and deterioration of their physical properties. Bleaching of the trimethine dyes in acidic or basic media is given in Scheme 3–28.

By addition of acid, loss of colour was observed and was also proposed by Katrizky.[109] This reaction is reversible since, after alkalisation of the solution, the deep red colour reappears. Supporting the proposed mechanism (Scheme 3–27). Under basic conditions this process is irreversible. The reaction of cyanines in alkaline environment, attack of the nucleophilic anion at C-2 is known,[110, 120, 121] and causes irreversible loss of the methine structure and destruction of the colour.



Scheme 3–28: Mechanism for bleaching of trimethine dyes in acidic and basic environment

Since the tetrahalogeno trimethine dyes were unstable for long periods of time in alkaline solution alternative ways for improving their stability were searched for.

3.2.2.2.5. ^{1}H NMR spectra of 5, 5', 6, 6'–tetrahalogeno trimethine dyes

In figure 3–15 (a) the ^{1}H NMR spectra of trimethine **104** is shown and assigment of its structure is given. The symmetry of the molecule causes the four aromatic protons to give two sharp singlets, which overlap with the triplet of the meso–positioned proton 11. Its large coupling constant with the two neighbour methine protons 10 and 10' of 13.4 Hz is typical for these dyes. For better illustration that region is shown in expanded form in Figure 3–15 (b).

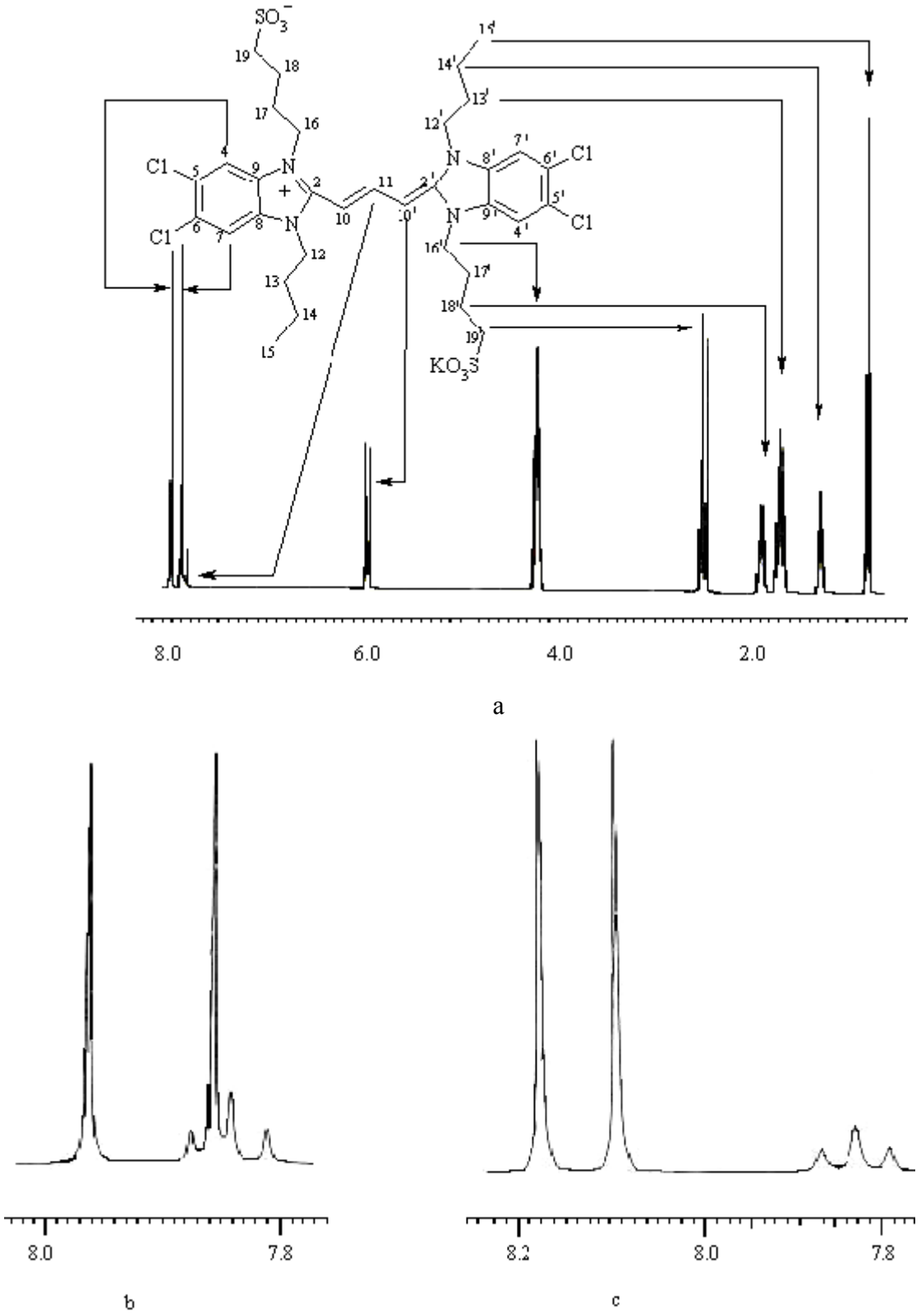


Figure 3–15: (a): ^{1}H NMR spectra of tetrachloro–dye **104** in DMSO (d_6); (b): expansion of the signals between 7.7 and 8.0 ppm; (c) expansion of the ^{1}H NMR spectrum (DMSO-d_6) of the tetrabromo–trimethine **106** between 7.8 and 8.2 ppm

The delocalisation of the positive charge in the bisbenzimidazolo trimethine is so pronounced, that all four *N*–CH_2 (12,16, 12' and 16') units give triplets with the same chemical shift (δ = 4.29 ppm). Another proof for the high symmetry of the molecule is the missing of differences in all signals of the alkyl chains, bound to both benzimidazolic units. Methyl groups 15 and 15' give only one triplet for 6 hydrogen atoms at 0.91 ppm and the neighbouring methylene groups 14 and 14' give a clean sextet (δ = 1.35 ppm). These results correspond to the published analytical data by Pawlik *et al*.,[123, 146] although their spectral interpretation appears to be incorrect.

A section of the ^{1}H NMR spectrum of the tetrabromo–analogue **106** is shown in Figure 3–15 (c). The four bromine substituents cause a down–field shift in expanded form towards the aromatic protons, in accordance with the small difference between their electronegativity and that of the chlorine atoms. The meso–proton remains in the same region and in this case is not overlap.

3.2.2.2.6. Synthesis of meso–substituted benzimidazolotrimethine 107

The synthesis of meso–phenyl substituted trimethine **107** was performed to improve the stability of the methine dyes by introduction of a bulky substituent. The reaction was performed again analogously to De Rossi *et al.*[40a] by coupling of a methylene base **101** with α,α,α–trichlorotoluene **100**. In this case the process is much slower, probably due to problems at the last stage, *i.e.* the formation of the methine chain by dehydrochlorinantion. The chlorine atom is strerically hindered by the phenyl ring, and the C–Cl bond is stronger than the C–I one (Scheme 3–27). Refluxing the reaction mixture for 5 h did not improve the yield.

Dye **107** has a very good solubility in organic solvents and aqueous mixtures, causing very low yields (8 %) during hot extraction and recrystallisation, furthermore large amounts of by–products are produced.

The dye shows no *J*–aggregation in any solvent mixture and in the present of ionic additives, probably due to the diminished planarity of the molecule and reduced conjugation. Because of these unsatisfactory results other alternativities had to be developed.

3.2.2.3. Synthesis of trimethine dyes with bissalicylic acid end groups

The aim of the introduction of salicylic acid end groups was to produce two additional acidic groups, which would be more attractive for deprotonation, resulting in a polyanionic dye. This should protect the methine chain and ensure higher stability against the aggressive alkaline environment. Another advantage could be the formation of an additional "ring" formed by an intramolecular hydrogen bond both in protonated and deprotonated forms between the carboxylic group and the hydrogen of the phenol:

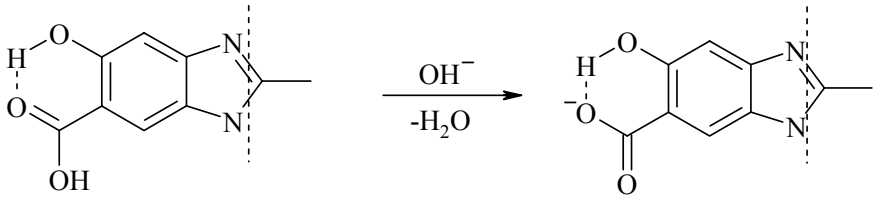
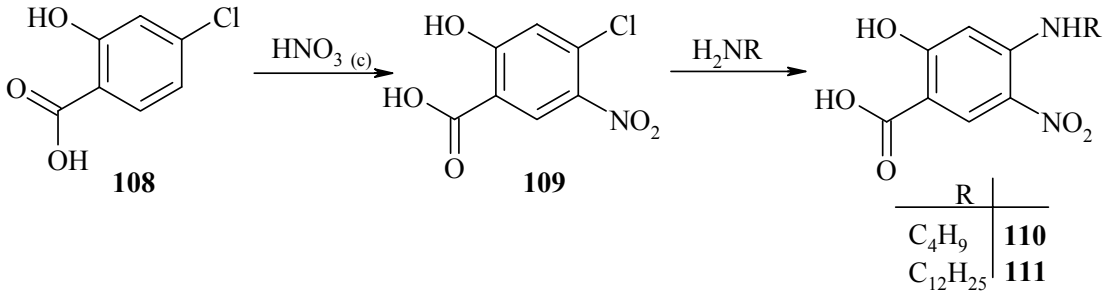


Figure 3–16: Formation of an intramolecular hydrogen bond in the salicylic acid end groups before and after deprotonation

It is also concerable that the intramolecular hydrogen bond formation could increase the planarity of the whole molecule. This effect would improve the aggregation properties of trimethine dye. On the other hand these new substituents could destroy the symmetry of the horizontal axis and the delocalisation of the electron density in the dye molecule.
Two derivatives of this type were synthesised with a *n*–butyl and subsequently a *n*–dodecyl substituent at the 1–nitrogen atom of the benzimidazolic nucleus. The preparation follows the same scheme as described for tetrahalogeno trimethine dyes, with some specific differences reasonable for this particular functionality.

3.2.2.3.1. Synthesis of 4–*N*–alkylamino–5–nitrosalicylic acid 110 and 111

The synthesis of the precursor for benzimidazole derivative **110** and **111** started from 4-chlorosalicylic acid **108**, which was first nitrated and then *N*–alkyl arylated:



Scheme 3–29: Synthesis of 4–*N*–alkylamino–5–nitrosalicylic acid derivatives

For the nitration step acetic acid was preferred as a mild solvent to promote the nitrosyl cation formation instead of sulphuric acid as described in the literature.[121] The stronger acid is not required, the reactivity is ensured by the powerful activating effect of the hydroxyl group in electrophilic substitution.[124] The sulphuric acid can act as an oxidising agent and could contribute to an undesired substitutions.

N–arylation was performed as described in section **3.2.2.2.1**. The reaction details are shown in Table 3–7:

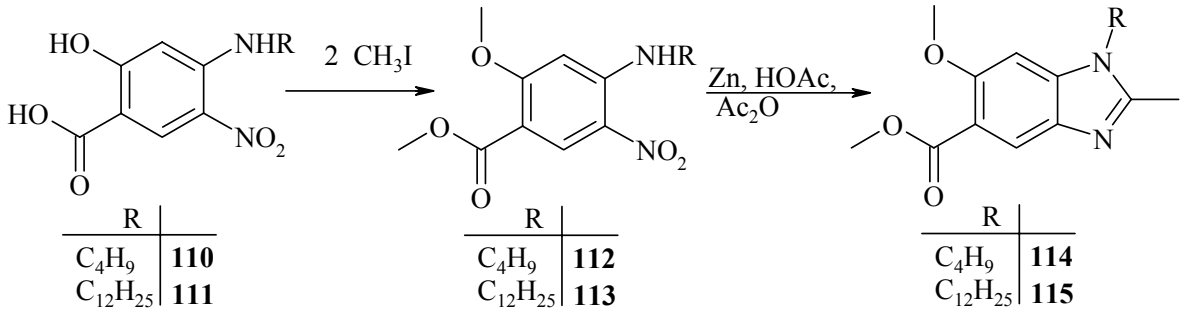
Table 3–7: Synthesis of 4–*N*–alkylamino–5–nitrosalicylic acid derivatives

Compound	React. time/h	Yield/ %	m. p./ °C	Solvent for recryst.
110	45	54.0	216–218	HOAc
111	100	50.3	130	MeOH

Compound **110** was prepared after 16 h under reflux, compared with 45 h for the same *n*–butylamine given in the literature.[40a] The synthesis of the *N*–dodecyl derivative **111** required more than twice the reaction time with similar success (50 % yield). The effect of the hydroxyl group is opposite and the phenyl ring is more or less deactivated for the nucleophilic attack of the amino group. Probably the use of catalytic amounts of copper and copper (I) compounds could improve the yields.

3.2.2.3.2. Synthesis of salicylic acid–derivatised benzimidazoles

The direct reductive cyclisation of compound **110** to obtain the benzimidazole derivative was unsuccessful. Besides 1,2–dichloroethane, toluene and chlorobenzene were tried as solvents for the reaction but only traces of the product were isolated. Darkening of the solutions was observed, caused presumably by oxidation of the target compound. To avoid this process both hydroxyl groups were protected as methyl ether and ester, respectively; with this variation the synthesis worked well.



Scheme 3–30: Synthesis of 1–alkyl–6–methoxy–2–methyl–5–methylmethanoate benzimidazoles; R = C_4H_9 or $C_{12}H_{25}$

Further *in situ* reduction with Zn/HOAc and subsequent cyclisation with Ac_2O afforded benzimidazoles **115** and **116**. Toluene was chosen as the solvent and the final neutralisation was performed with concentrated ammonia in order to prevent the removal of the methyl ester–protective group. The reaction details, yields and melting points are given in Table 3–8:

Table 3–8: Synthesis of salicylic acid derivatised benzimidazoles

Compound	R	React. time/h	Yield/ %	m. p./°C	Solvent for recryst.
112	Butyl	5	83	130	EtOH/HOAc
113	Dodecyl	5	87	114	EtOH
114	Butyl	40	85	107	Toluene
115	Dodecyl	20	97*	–	n–Hexane**

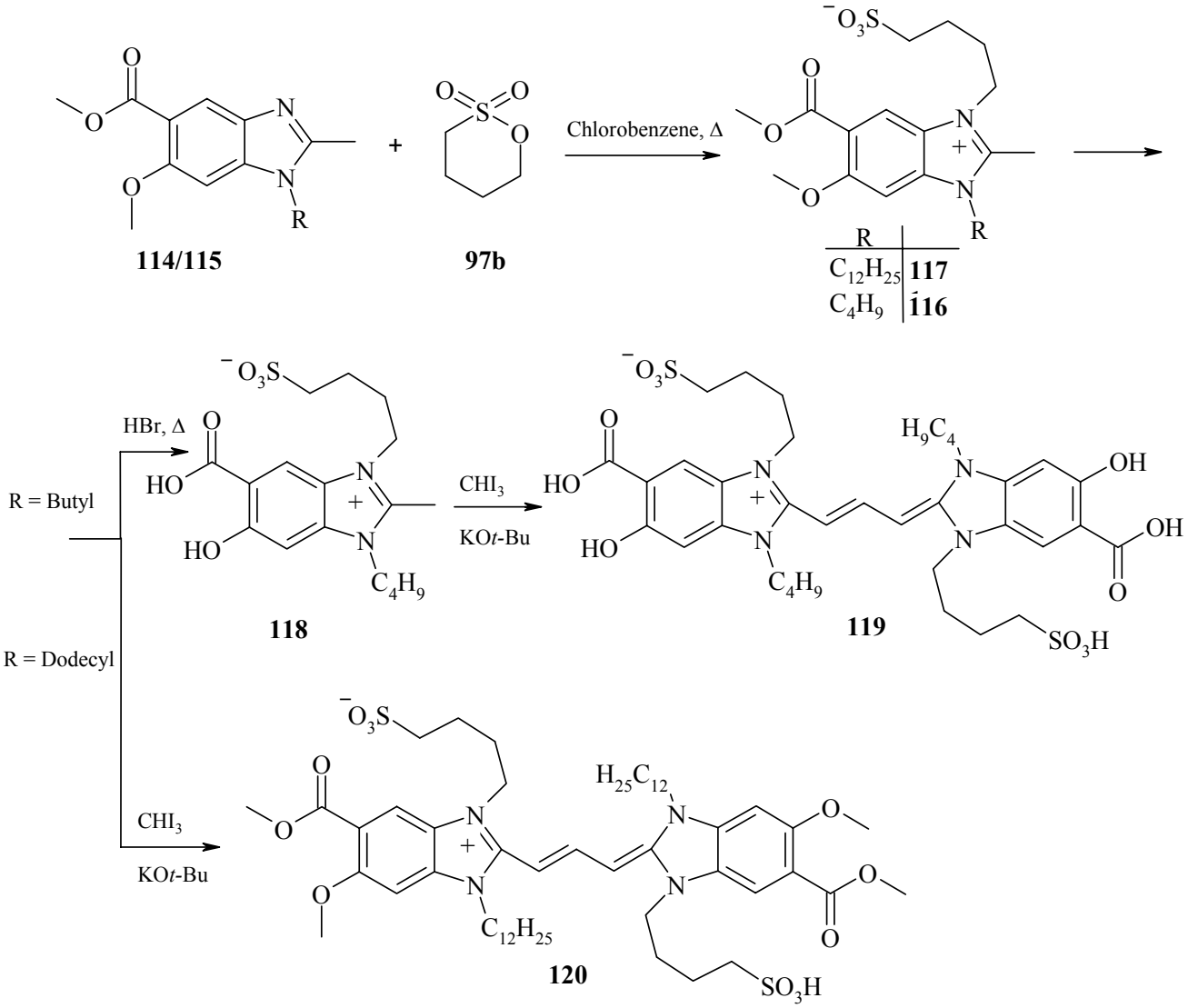
(*–Raw yield; **–freeze in liquid nitrogen)

No satisfactory elemental analyses for compound **115** was obtained as the long alkyl chains turned it into a heavy oil, that retains solvents even after one week of drying *in vacuo* at 50 °C. Sufficient purity was achieved after dissolving it in *n*–hexane and freezing the solution in liquid nitrogen. Subsequently the flask was allowed to warm up slowly (to app. –30 to –50 °C) and then the solid was quickly filtered through a pre–chilled funnel. Compound **115** appeared as dirty white plates at minus temperatures and changes again to a heavy oil at room temperature, the derivative became darker on standing.

Compounds **112** and **113** were obtained in very good yields (84 and 87 %) as shiny yellow plates, soluble in polar and unpolar solvents.

3.2.2.3.3. Synthesis of salicylic acid–derivatised benzimidazolotrimethines

The synthesis of salicylic–derivatised trimethines was carried out as described above for the tetrahalogen–cyanine dyes. The synthetic route is shown in Scheme 3–31:



Scheme 3–31: Preparation of salicylic–derivatised benzimidazolotrimethines **119** and **120**

The quaternisation of benzimidazoles **114** and **115** was carried out in chlorobenzene and the reactions were completed in shorter time, compared to the previous methylene bases (see above). This reactivity increase is caused by the electron-donating effect of the methoxy group. Another difference is that these betaines are more soluble in the reaction solution and have not settled down as sediment during quaternisation. The butyl–derivative forms a viscous mass after cooling to 10 °C, and provides product **116** as white prisms after recrystallisation from EtOH. The *N*-dodecyl derivative **117** was obtained as white plates after

precipitating it from the cooled solution with diethyl ether. Both compounds possess good solubility in DMSO and the NMR measurements were performed at room temperature.

Deprotection of substance **116** was performed according to Nakazawa and Sawahara.[126] The hydrolysis of the cyano group in HBr solution resulted in the corresponding carboxylic acid function with similar benzimidazole substrate. It is of cource well known that esters can be saponified in alkaline as well as in acid media[127] and aqueous HBr is a very good cleavage reagent for ethes.[128] The longer reflux time is typical for that reaction, and is required for the deprotection of the ether group.

Attempts to obtain trimethine dye **119** showed many difficulties – excess of KO*t*Bu was required to obtain the active methylene base, the reaction took place very slowly, the typical cyanine colour appeared only at heating over 60 °C and many by–products were observed by RP–TLC analisis. After 8 h of refluxing in EtOH the process was stopped. The attempted purification by chromatography and recrystallisations resulted in mixture of compounds or decomposition products. The desired *J*–aggregation under alkaline conditions was not observed. The dye changed its colour batochromically only upon addition of acetone in aqueous ethanol solutions. On standing the red colour disappeared slowly.

For this reason demethylation of the betaine **117** was not carried out - the protected methylene base was directly coupled with iodoform to form dye **120**. The purification by FC with MeOH/$CHCl_3$ as eluent gave satisfactory NMR and MS–spectra, but no elemental analysis could be obtained. The dye was very well soluble in polar and nonpolar organic solvents, but it was not possible to recrystallise it. Moreover, it aggregated like dye **119** in acetonic mixtures. The results are shown in Table 3–9:

Table 3–9: Synthesis, yields and melting points of salicylic acid–derivatised benzimidazolobetanines and trimethine dyes **116-120**

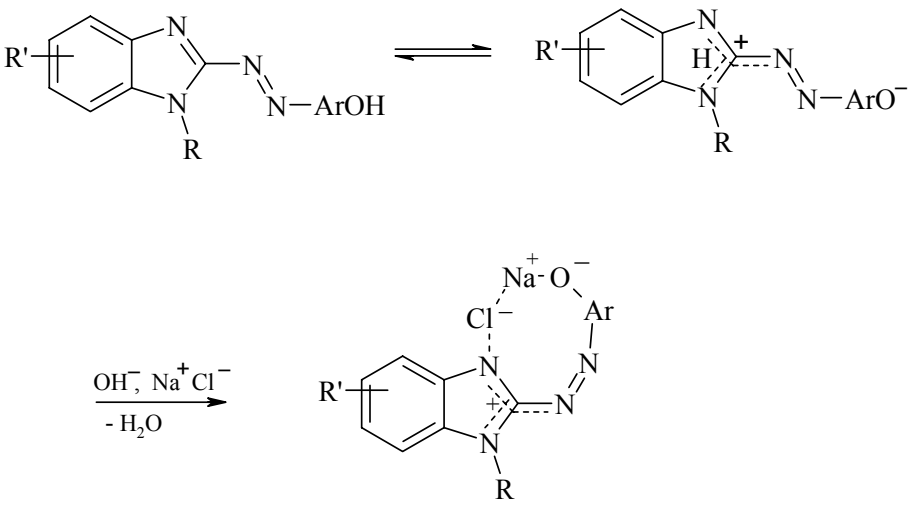
Compound	React. time/h	React. temp/°C	Yield/ % theor.	m. p./ °C	Purification
116	3	reflux in C_6H_5Cl	72	262	recryst. from EtOH
118	48	reflux in 32 % HBr	73	310	boiling in acetone
117	10	reflux in C_6H_5Cl	86	198–200	precipitation from ether
119	8	reflux in EtOH	–	–	–
120	2	RT/ MeOH	31*	292	FC (MeOH/$CHCl_3$ 1/1)

(*–raw yield)

In summary, the salicylic acid–end groups did not improve the stability of the trimethine dyes. However, *J*–aggregation–sensitivity towards chloride was lost probably due to the loss of the symmetry of the dyes.

3.2.3. Complex–forming benzimidazolo–azo dye 122

It is well known that quaternery guanidium compounds are effective receptors for anions.[129] Another advantage is that their cations are quite independent from the pH with regard to the pK_a (13.5) of guanidine.[130] The guanidinium moiety plays the role of a Lewis acid by interaction with the anions (resp. Lewis bases). A typical structure is represented by 2–azo–benzimidazolo dyes **7**. Diazotisation of 2–amino–1–methylbenzimidazole **121** and subsequent coupling with hydroxy–aromatic compounds lead to products with a zwitterionic structure:



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Scheme 3–32: Proposed zwitterionic structure of 2–azo–benzimidazolo dyes **7** and its complex–formation, R' = common substituent

4–Methyl–2–(1–methylbenzimidazol–2–ylazo) phenol **122** was synthesised by Kolodjajnaja *et al.*[131] by coupling of diazotated 2–amino–1–methylbenzimidazole **121** with *p*–cresol in HOAc/water. With regard to the weak basic character of the amino group, the diazotisation is performed in concentrated phosphoric acid with solid $NaNO_2$ at –10–15 °C. The yield was better as given[131] - 33 % versus 18 %. The performed analysis has shown that the proposed structure proposed by the Russian authors was incorrect. Obviously, the electrophilic attack

occurs at the activated *o*–position in the phenolic nucleus, and not at the *m*–position. The formation of a protonated hydroxyl group (demethylation in the case of methoxy instead hydroxyl group has been reported[131]) could be possible under such strongly acidic conditions. Consequently, the methyl substituent could play an activating role, but in this case the nucleus would be, in principle, deactivated for electrophilic attacks.

Dye **122** was shown to possess very interesting optical properties *i.e.* when the orange–yellow acetonic solution was applied to the TLC plate (both SiO_2 and Al_2O_3) the colour of the spot changed to blue. Such dramatic colour change cannot be due to azo–hydrazono tautomerism only, but the dye could form complexes with the polar molecules of the plate. Other evidence for complexation is provided by the observation that the deprotonated form has a violet colour and becomes blue only upon addition of salts. The X–ray analysis confirmed the hypothesis showing that complexation with ethanol readily occurs:

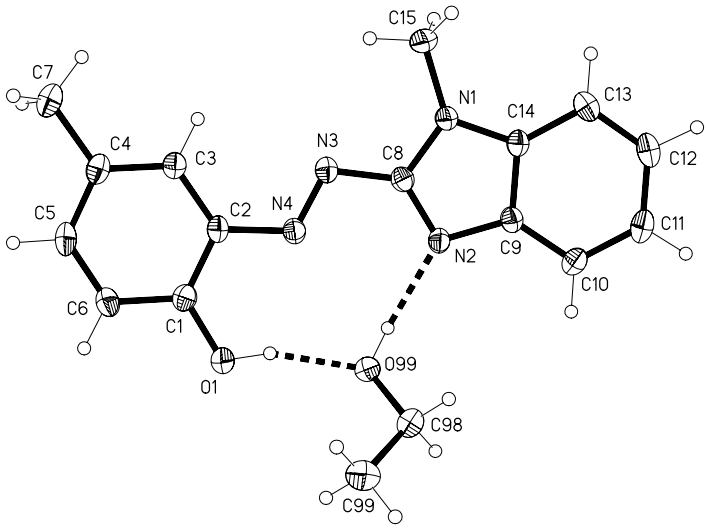


Figure 3–17: Structure of dye **122** in the crystal, obtained from EtOH. Radii are arbitrary.

The positively charged hydrogen atom of the hydroxyl group of EtOH (Fig. 3–17) forms an intermolecular hydrogen bond with the imidino nitrogen from the benzimidazole. The cycle is closed by the negatively charged oxygen through another intermolecular hydrogen bond with the hydrogen atom of the phenolic group of the dye. That dye tends to form complexes with various polar molecules (polar surface of the TLC plate).

3.3. Optical properties

The optical properties of molecules are characterised by their electronic spectra, which can be divided in two main types: absorption and emission spectra. UV/vis absorption spectra are the result of the excitation of electrons from the ground state to a higher energy level. The ultraviolet absorption zone (UV) occurs in the range from 100 to 400 nm, visible (vis) from 400 to 800 nm and beyond 800 nm begins the infra red (IR) zone of the spectrum. The electrons in the organic molecules are of σ–, π– and p-nature; they participate in covalent bond formation or remain nonbonding AO-orbitals. Possible transitions are $\sigma\rightarrow\sigma^*$, $\pi\rightarrow\pi^*$, which are also called N–V transitations and $n\rightarrow\sigma^*$ and $n\rightarrow\pi^*$, called N–Q transitations. N–V transitations possesses the highest intensity, and contribute most strongly to the electronic spectra of organic molecules. The $\sigma\rightarrow\sigma^*$ excitations are typical for saturated hydrocarbons and are in the far UV–range, from 100 to 200 nm, whereas the $\pi\rightarrow\pi^*$ excitations are in the near UV (250–400 nm) and vis range, because of their higher ground state energies. Conjugation between π–orbitals decreases the energy gap between ground and excited states and shifts the energy transfer to longer wavelengths. Such conjugated chains are called chromophor chains. When the ends of the chromophor chain are linked to an electron rich funtional group and a group, which is deficient of electrons, respectively the so-called bathochromic shift (or red shift) to longer wavelength is induced. This transition is also called "charge–transfer" (CT), since both end–groups become polarised. Other factors such as coplanarity of the molecule and solvatochromism also play an important role in that process.
Since changes in the environment influence the CT-transition some classes of dyes can be used as optical sensors for these changes.

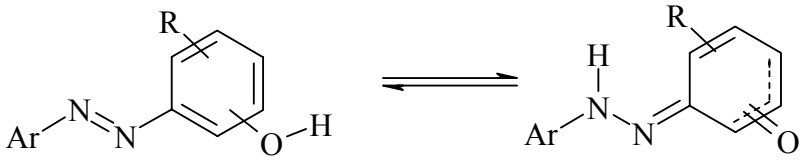
3.3.1. Optical properties of pH–indicator azo dyes

The chromophor in azo dyes is formed by two or more aromatic nuclei, connected by the azo (–N=N–) bridge. The colour of monoazo dyes is usually yellow to orange depending on the substituents in the aromatic parts, which must possess at least an electron-donating group in the first and at least one acceptor in the second aromatic substituent.
Optical properties can be influenced by solvent, temperature, light *etc*., which all effect different structural properties of the dyes such as *Z/E* isomerism, rotational equlibria (conformation), tautomerism *etc*.

3.3.1.1. UV/vis–spectral analysis of the tautomer equilibrium

3.3.1.1.1. Hydroxyazo–ketohydrazono tautomerism

Compounds whose structures differ markedly in arrangement of atoms, but which exist in easy and rapid equilibrium, are called tautomers. The most common kind of tautomerism involves structures that differ in the point of attachment of a hydrogen substituent. The availability of a labile proton in the molecule of hydroxyazo dyes, determines their existence in two forms – the hydroxyazo and ketohydrazone tautomer respectivelly (Scheme 3–33)



Scheme 3–33: Hydroxyazo–ketohydrazono tautomerism of azo dyes

Hydroxyazo dyes, capable to undergo azo–hydrazone tautomerism have to bear a OH-group conjugated with the azo group, *i.e.* they are *o*– and *p*–hydroxyaryl azo compounds. Meta–isomers do not possess this property. The factor, which causes the biggest influence on the equilibrium, is the thermodynamic stability of both forms. This is quantified by the resonance stabilisation energy (RSE), and dyes exist in the form, whose resonance energy is lower. For better illustration, data given from Gregory and Gordon,[132] are listed bellow:

Table 3–10: Resonance stabilisation energy (RSE) of aromatic compounds and their quinone derivatives

Substance	RSE, [kJ·mol^{-1}]	Difference
benzene	150.5	134
1,4–benzoquinone	16.5	
naphthalene	255	90.7
1,4–naphthoquinone	164.3	
anthracene	349	3
9,10–anthraquinone	346	

For example the loss of the aromatic structure in azophenol dyes cannot be compensated by the RSE of the hydrazone–form and these compounds therefore exist predominantly in the hydroxazo–state. For hydroxynaphthylazo dyes the RSE between the hydrazone–structure in the azo–tautomer is smaller and these dyes are normally present in higher percentage in the equilibrium between both forms. Finally, in azoanthrol the difference is very small and these derivatives exist totally in their hydrazone form.

3.3.1.1.2. UV/vis–spectra of the azo–hydrazone tautomers

UV/vis spectroscopy is one of the most powerful physical method for determination of azo–hydrazonium tautomeric equilibria in solution. The first quantification of this phenomenon was performed by Kuhn and Bar.[133] The ratio of both tautomeric forms in different solvent mixtures for several main classes of phenylazo–hydroxynaphthols was studied in details by Antonov and Stoyanov.[134] Solvents can exert a profound influence on tautomeric equilibria. Generally, more polar solvents favour the hydrazone form whereas in less polar solvents the azo form is favored.[132] Other factors such as the substituents, temperature, pH *etc*. play important roles.

The position of the hydroxyazo–ketohydrazone equilibrium in different solvents of the synthesised acetal dyes **18**, **41**, **40**, **39** and **31a** are shown in Figures 3–2–6.

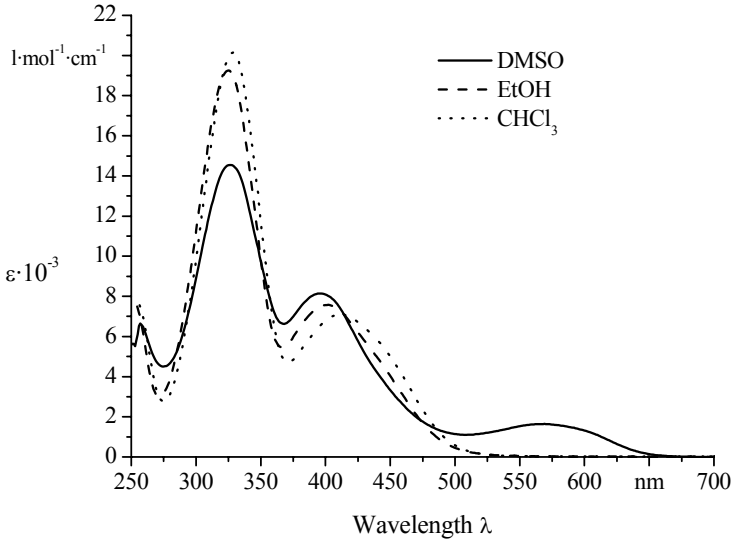


Figure 3–18: UV/vis spectra of **18** in different solvents.

Figure 3–18 shows the UV/vis spectra of the *p*–cresol azo dye **18**. For phenylhydroxy azo dyes it is known that they exist predominantely in their azo form (Table 3–10). However, dye **18** shows an untypical hydrazone long–wavelength band at λ_{max} = 569 nm in the aprotic polar solvent DMSO. The absorption maxima is red–shifted more than 150 nm with respect to the azo–form. In unpolar solvents ($CHCl_3$) and protic polar (EtOH) only the hydroxy–azo form was observed. Its absorption maxima possesses reverse solvatochromism – in DMSO it appeared at the shortest wavelength - 396 nm (ε = 8 000 l·mol^{-1}·cm^{-1}. In EtOH it is at 402 nm (ε = 7 500 l·mol^{-1}·cm^{-1} and is the most red–shifted in $CHCl_3$ - 410 nm (ε = 7 000 l·mol^{-1}·cm^{-1}. Another charcteristic property is, that together with the bathocromic shift, the peaks became narrowed, *i.e.* they possess hypochromism. Probably this is due to the more pronounced conjugation in the azo form, caused by the increased percentage of intramolecular hydrogen bond formation in the unpolar solvents. On the other hand the rotation around the C–N bond at the other substituent can cause a poorer CT–conjugation leading to the hypochromic character of the maxima.

Compared to the phenol–azo dyes the naphthol–azo dyes shows a higher mobility in the azo–hydrazone tautomerism.

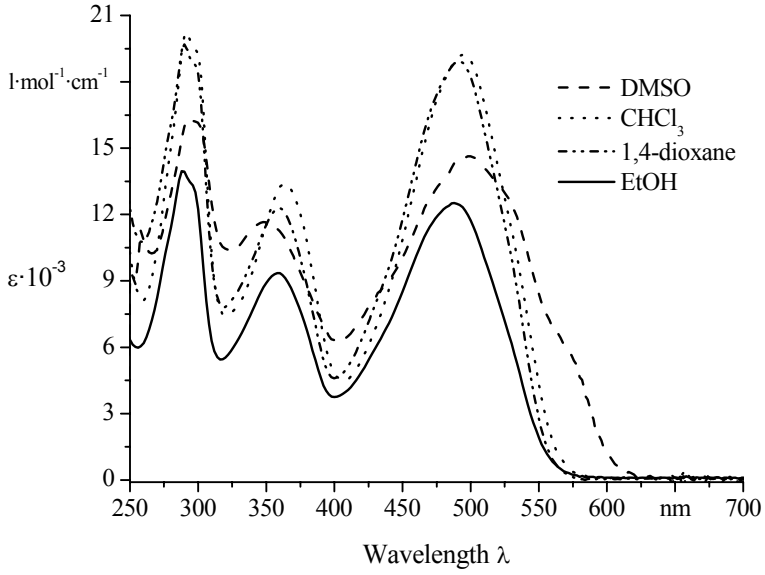


Figure 3–19: UV/vis spectra of 2–phenylazo–1–naphthol dye **41** in different solvents at conc. $3.5 \cdot 10^{-5}$ M ($CHCl_3$, 1,4–dioxane and EtOH) and $3.6 \cdot 10^{-5}$ M (DMSO)

Dye **41** exists predominantly in its hydrazone form in all solvents with absorption maxima ranging from 489 nm (EtOH) to 500 nm (DMSO). The expected absorption of the azo–form (415–430 nm) is only recognisible in DMSO (shoulder at 429 nm), in the other solvents is

negligible. These results correspond well with those reported by Antonov and Stoyanov (UV/vis measurements of 2–phenylazo–1–naphthols).[134a] Interesting is the long–wavelength shoulder in DMSO at 560–570 nm. This absorption can be assumed to belong to dimeric structures, which are given by Zollinger[135] for comparable *o*–hydroxynaphtyl azo dyes. Dye **41** does not show distinct solvent dependence, because it is stabilised to a significant extent by the six–membered ring formed by an intramolecular hydrogen bond which dominates the hydrazone–form. Different behaviour was observed for the *o*–dye **40**:

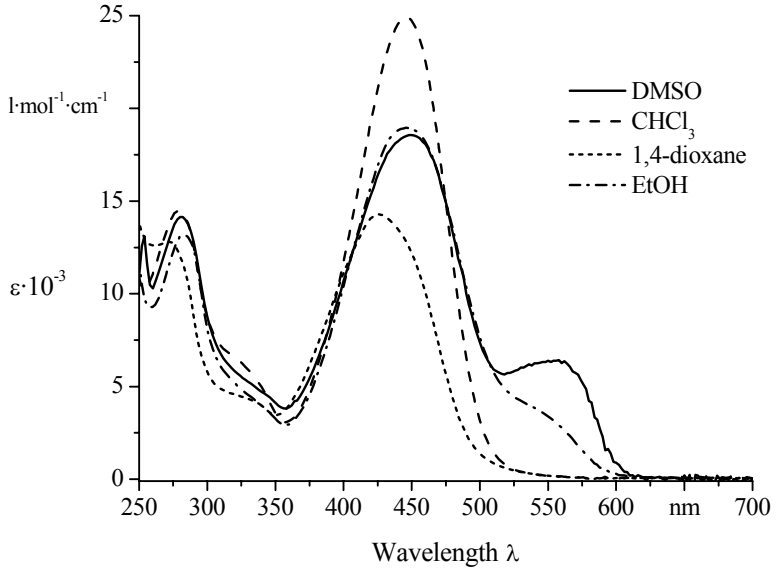
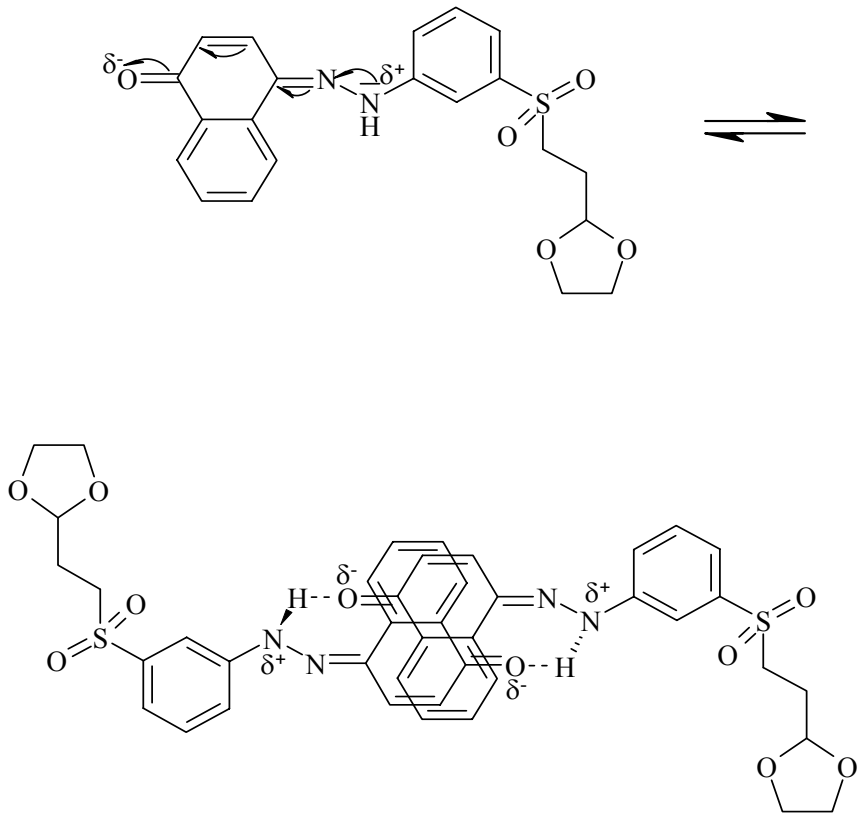


Figure 3–20: UV/vis spectra of 4–phenylazo–1–naphthol dye **40** in different solvents at conc. $3.9 \cdot 10^{-5}$ M ($CHCl_3$ and 1,4–dioxane) and $3.7 \cdot 10^{-5}$ M (EtOH and DMSO)

Dye **40** exists predominantly in the hydroxyazo–form in dioxane (λ_{max} 426 nm). Other solvents favour the hydrazone form with a bathochromically shifted maximum (λ_{max} 445 nm). In protic polar solvents such as EtOH the dimer structure appeared at 540 nm as a shoulder and a clear maximum is seen in aprotic polar solvents such as DMSO at 550 nm. The higher affinity to dimerisation can be explained with the greater distance between positively (N) and negatively (O) charged atoms in the resonance structure, which are more stable and allow additional double intermolecular hydrogen bond formation (Scheme 3-34).



Scheme 3–34: Proposed dimerisation of *p*–hydroxynaphthylazo dye **40**

The most highly resolved absorption spectrum appears in bipolar aprotic solvents such as DMSO. This stabilises the hydrazone form and does not favour intermolecular hydrogen bonds in the dye molecules such as protic solvents like EtOH. In this latter case exists a more stabilised, double intermolecular hydrogen bond charge–transfer structure, leading to a decrease of the total energy of the system and lowering n→π* excitation, explaining the long wavelength maximum at 550 nm.

Interesting is the strong absorption in $CHCl_3$, where the extinction coefficient ε reaches 25 000 $l \cdot mol^{-1} \cdot cm^{-1}$. The explanation could be that the dye occurs in 100 % in its hydrazone form without dimeric structures; according to Lambert–Beer's law the concentration causes this strong absorption.

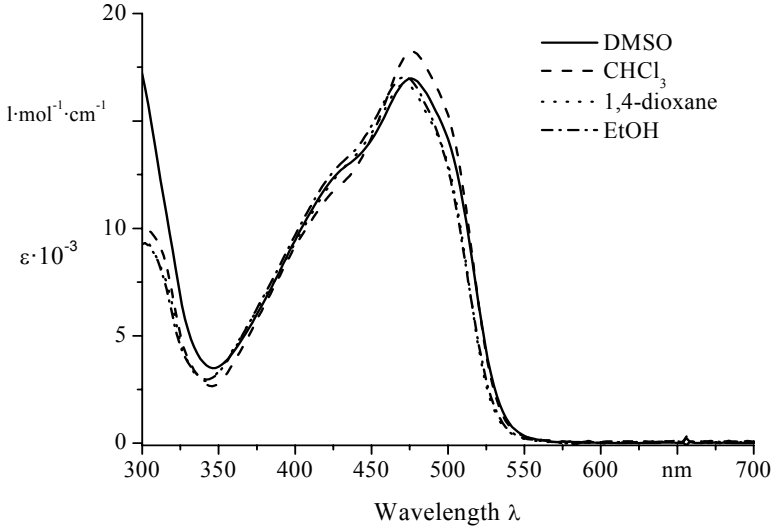


Figure 3–21: UV/vis spectra of 1–azo–2–hydroxynaphthyl alkylsulphone dye **39** in different solvents at conc. $3.4 \cdot 10^{-5}$ M ($CHCl_3$ and 1,4–dioxane) and $2.9 \cdot 10^{-5}$ M (EtOH and DMSO)

In Figures 3–21 and 3–22 are shown the UV/vis spectra of 1–azo–2–hydroxynaphthyl dyes **39** and **31a**. Here equilibria between hydroxyazo and ketohydrazone tautomers are observed in all solvents.

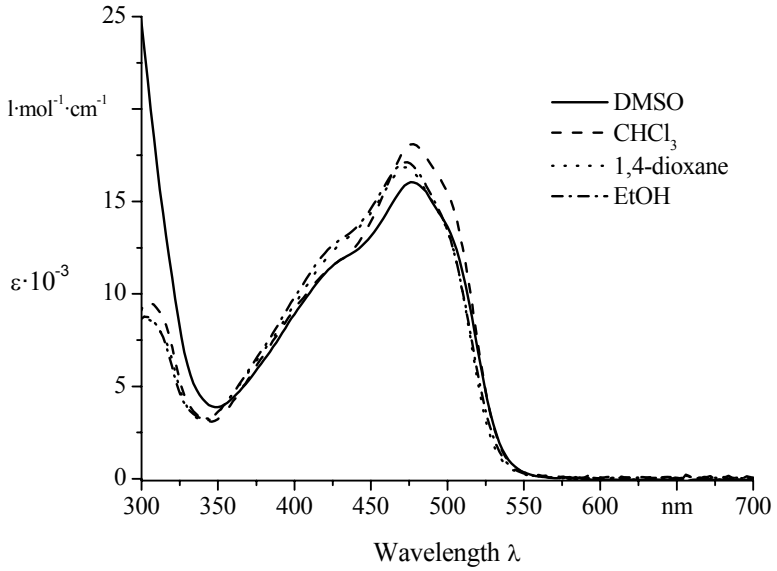


Figure 3–22: UV/vis spectra of 1–azo–2–hydroxynaphthyl sulphonamide dye **31a** in different solvents at conc. $4.0 \cdot 10^{-5}$ M ($CHCl_3$ and 1,4–dioxane), $3.3 \cdot 10^{-5}$ M (EtOH) and $2.4 \cdot 10^{-5}$ M (DMSO)

The absorption maxima are 425 nm and 475 nm, respectively, with less pronounced changes than in the α–naphtol azo dyes. Similar UV/vis investigations of 1–phenylazo–2–naphthol have been reported.[134b]

The sulphonamido–group did not influence the azo–hydrazone tautomerism, nor the absorption maxima significantly. The low concentrations of **31a** in DMSO prevent formation of dimers, which are seen as a shoulder at 501 nm. For *o*–hydroxyazo dyes the intramolecular hydrogen bond is also more stable and formation of dimers is hence not so strongly favoured as for the *p*–isomers.

3.3.2. Optical indicator properties

As mentioned above (section **1.3.1.1.)**, the indicator dyes must possess the following optical properties: either their absorption maxima must shift continuously batho– or hypsochromically, corresponding to the concentration changes of the measured species, or they must show two maxima the signals intensities of which change in accordance with the environmental changes of their surround. Another desired characteristic is an isosbestic point in the UV/vis spectra - a wavelength, at which the absorption of two substances, which can be converted into the another, remains unchanged.

3.3.2.1. UV/vis spectra of pH–indicators

For acid–base indicators protonated and deprotonated forms of the dyes are a function of the pH in the equilibrium. Thus, both forms can be determined by UV/vis spectra by their specific wavelength bands and absorption or fluorescence intensities. The first approach concerning the pH range, for which the colour change exists, was to measure the UV/vis spectra in different pH–buffer solutions.

3.3.2.1.1. UV/vis spectra of pH–indicator dyes in solutions

Wishing to minimise the concentration and polarity influence, and also to achieve good solubility in aqueous solutions, the dyes were dissolved in organic solvent (DMSO) and 1 mL of this aliquot was diluted to 10 mL with standard pH–buffer solutions 8–13 or 1 *N* KOH.

The UV/vis absorption spectra of the acetal–azo dyes **18**, **40** and **41** in different pH–buffer solutions are shown in Figures 3–23–25

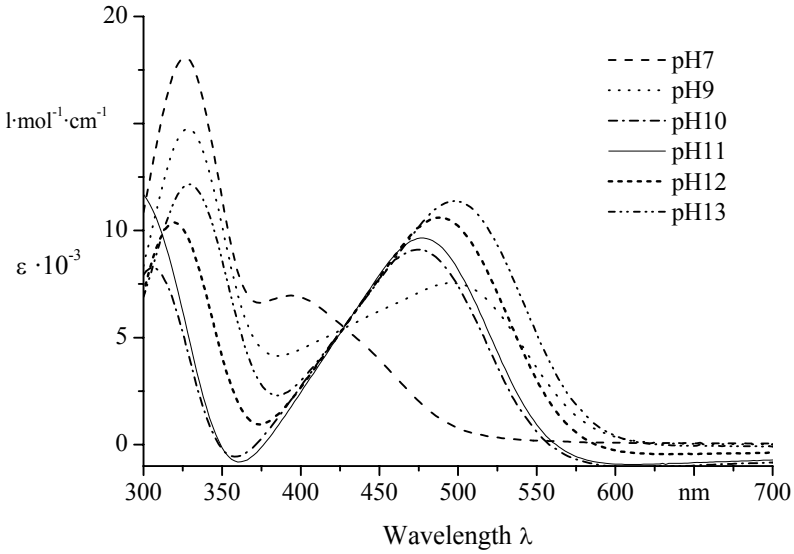


Figure 3–23**:** UV/vis spectra of *p*–cresol azo dye (**18**) at different pHs (dye conc. $4.5 \cdot 10^{-5}$ M)

Azo dye **18,** for which the OH-group is in o-position to the azo group**,** possesses excellent indicator properties within the alkaline pH–range (Fig. 3–23). The distinct maximum of its absorption spectrum is shifted both bathochromically and – to a lesser extent – hyperchromically with increasing pH. The molar extinction coefficient ε of the protonated form at 396 nm decreases from 7 000 to 4 400 $l \cdot mol^{-1} \cdot cm^{-1}$ at pH 9 to 2 700 and 2 000 $l \cdot mol^{-1} \cdot cm^{-1}$in the high alkalinity range - pH 11-13. The newly appearing maximum for the deprotonated form is shifted form 475 nm (ε = 9 000 $l \cdot mol^{-1} \cdot cm^{-1}$) at pH 10 to 478 nm (9 600 $l \cdot mol^{-1} \cdot cm^{-1}$) at pH 11, 498 nm (10 500 $l \cdot mol^{-1} \cdot cm^{-1}$) at pH 12 and 500 nm (11 300 $l \cdot mol^{-1} \cdot cm^{-1}$) at pH 13. Only the maximum at pH 9 is at 496 nm, but its intensity is much lower (7 500). A clear isosbestic point at 428 nm (5 400 $l \cdot mol^{-1} \cdot cm^{-1}$) exists, which is a significant advantage. There is an another absorption maximum at 325 nm, but it has no obvious relation to the pH.

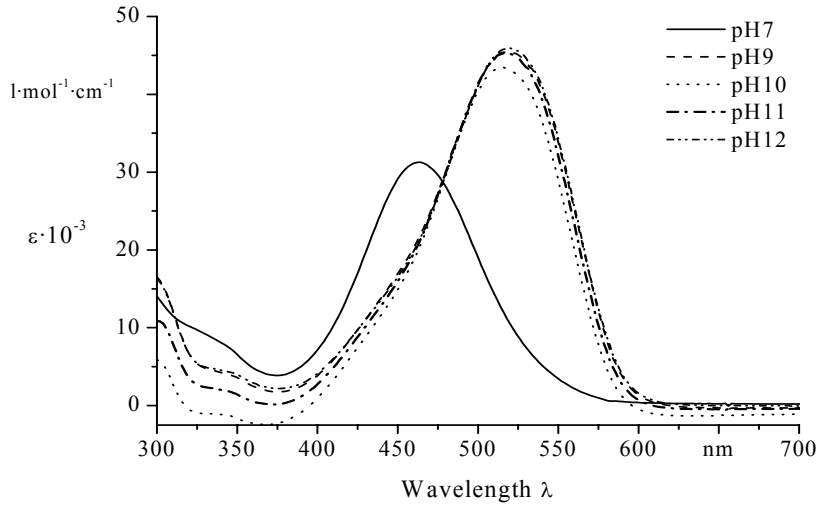


Figure 3–24: UV/vis spectra of *p*–α–naphthol hydroxyazo–dye (**40**) at different pHs (conc. $6.7 \cdot 10^{-4}$ M)

The other dyes do not show such a marked pH–dependence of their absorption spectra. The *p*–α–naphthol azo dye **40** has no possibility for intramolecular hydrogen bond–formation and the deprotonation is facilitated. Even at pH 9 the dye is almost deprotonated (λ = 513 nm) and further increasing of the pH leads only to very small batochromic shift - up to 520 nm at pH 12. The absorption spectrum at pH 13 is practically identical with that at pH 12.

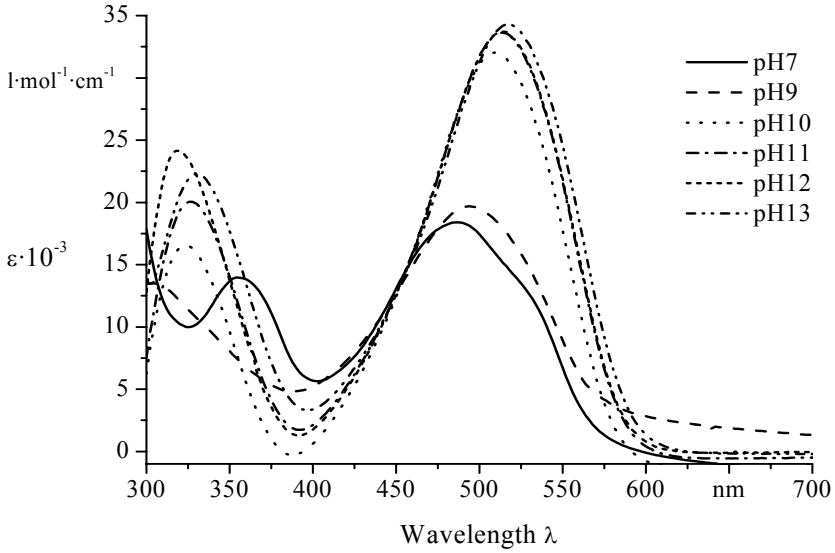
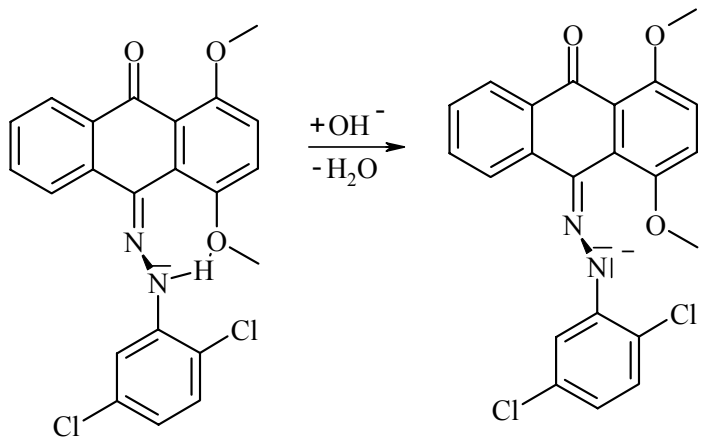


Figure 3–25: UV/vis spectra of o–α naphthol–azo dye (**41**) at different pHs (conc. $5 \cdot 10^{-5}$ M)

The differences in absorption intensities are also insignificant - ε = 43 400 $l \cdot mol^{-1} \cdot cm^{-1}$ at pH 9 and around 45 000 $l \cdot mol^{-1} \cdot cm^{-1}$ in highly alkaline environment. The isosbestic point for **40** appeared at 478 nm.

o–Hydroxyazo dye **41** exists as hydrazone tautomer with λ_{max} = 484 nm (ε = 18 200 $l \cdot mol^{-1} \cdot cm^{-1}$) and a shoulder of dimers at 520 nm (14 000 $l \cdot mol^{-1} \cdot cm^{-1}$) in neutral pH. At the slightly increased pH of 9 a new maximum appears at λ_{max} = 495 nm, but in this case is due to the intramolecular hydrogen bond, the extent of deprotnation is very small. Further increase of pH is reflected in the absorption spectrum of dye **41** by hyperchromic shifts rather than bathochromic ones. At pH 10 the maximum is found at 508 nm, pH 11 and 12 - 513 nm and at pH 13 - 517 nm and almost equal molar extinction coefficients - ε for the last 3 pHs are around 34 000 $l \cdot mol^{-1} \cdot cm^{-1}$.

With these hydroxyphenyl– and naphthyl–azo dyes the pH–range from 9 to 13 was covered. Best results were obtained for *p*–cresol azo dye **18**. For optical detection in the higher alkaline region, anthraquinone hydrazo dyes **60** and **62** were synthesised. The deprotonation in these dyes occurs at higher pHs, because of the influence of several factors. Firstly both electron–donating methoxy groups decrease the electron–withdrawing power of the carbonyl group. For those dyes it is known (Table 3–10), that they exist totally in their hydrazone form. Hence, deprotonation will occur at the nitrogen atom. Furthermore the ArNH–group is much weaker acid than ArOH, requiring higher concentration of hydroxyl ions (respectively pH).



Scheme 3–35: Deprotonation of anthraquinonimine dye **60**

Thirdly, a weak intramolecular H–bond between the NH–proton and the oxygen atom from the methoxy group C-4 can be assumed (Scheme 3–35), which gives an additional stability of the N–H bond.

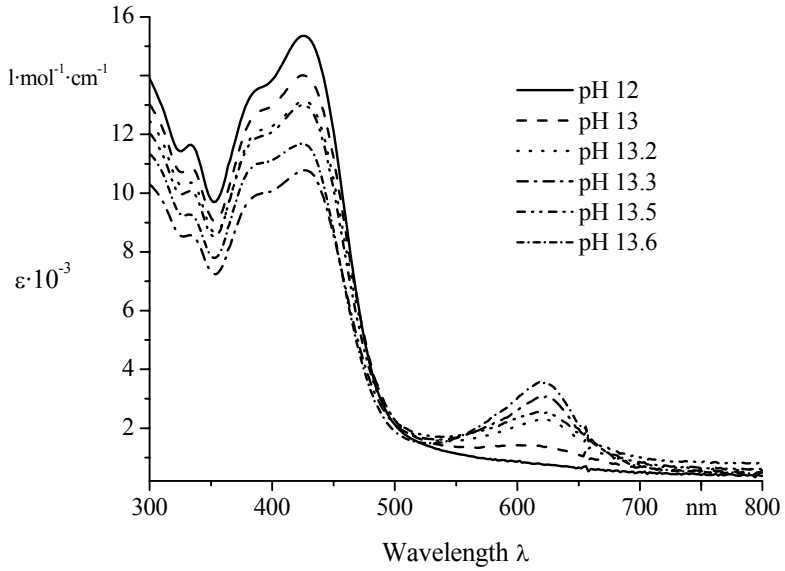


Figure 3–26: UV/vis spectra of anthaquinone monophenylhydrazone dye **60** at different pHs, conc. $3.94 \cdot 10^{-5}$ M

All these propositions were proved by UV/vis – spectra of dye **60** at different alkaline pHs. Up to pH 12 the spectra of the dye were unchanged and only the maxima of both chromophore chains were observed. The first band is caused 1,4-dimethoxyanthraquinonimine at 425 nm (ε = 15 000 $l \cdot mol^{-1} \cdot cm^{-1}$) and the second by the dichloroaniline part of the dye as a shoulder at 385 nm (ε = 13 500 $l \cdot mol^{-1} \cdot cm^{-1}$). At pH 13 a new bathochromically shifted maximum was observed at 620 nm (ε=1400 $l \cdot mol^{-1} \cdot cm^{-1}$), which grew with further increase of alkalinity of the solution. The absorption is very sensitive to small changes in pH in the region 13 – 13.6 which is very important for the practical use. Dye **60** shows a dependence of the ionic strength of the solvent mixture and the indicator properties change smootly up to pH 13.6. At higher pHs there irregular dependencies were observed. This could be due to the solubility of **60** in the aqueous solvents – it does not possess hydrophilic polar groups and subsequently saturation occurs.

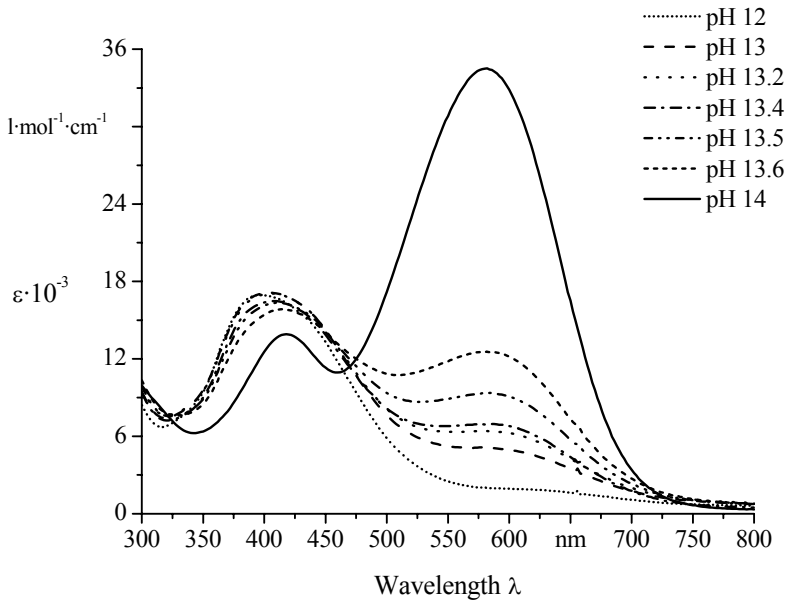


Figure 3–27: UV/vis spectra of anthraquinone monophenylhydrazone dye **62** at different pHs, conc. $3.7 \cdot 10^{-5}$ M

The 2,4–dinitro substituted dye **62** also changed its colour in the pH range from 13 to 14. At pH 12 only one maximum was clearly recognisable at 395 nm (ε = 17 000 l·mol^{-1}·cm^{-1}), corresponding mainly to the 2,4–dinitroaniline chromophor. The anthraquinonimine part can be assumed to cause a long shoulder at the longer wavelengths, reaching beyond 500 nm. Increase of the pH to 13 caused the appearance of a new maximum at 582 nm (ε = 5 000 l·mol^{-1}·cm^{-1}). The higher pHs are very well correlated with the hyperchromic effect of the longer wavelength maximum – the molar extinction coefficient increases from 7 000 l·mol^{-1}·cm^{-1} at pH 13.3, 9 000 l·mol^{-1}·cm^{-1} at pH 13.5, 12 700 l·mol^{-1}·cm^{-1} at 13.6 and finally drastically to 34 500 l·mol^{-1}·cm^{-1} at pH 14, respectively. The shorter wavelength maximum also responded the pH–changes. It was shifted bathochromically from 395 nm at pH 12, through 402 nm at pH 13 to 418 nm at pH 14. Simultaneously with these shifts a hypochromic change of these maxima was observed - from 17 000 to 14 000 l·mol^{-1}·cm^{-1}. These optical characteristics make dye **62** a good photometrical sensor for extremely high alkaline conditions.

3.3.2.1.2. pH–indicator properties of covalently bound polymer dyes

The pH–dependencies of dye–polymer composites were obtained for thin membranes, which were exposed to different alkaline pH–buffer solutions. The membranes require 5–10 minutes initially to absorb water and then the process occurs within seconds. Unfortunately, the composites were soluble only in DMF and from this point of view the preparation of spin–coated membranes was impossible. Hence, the membranes were not evenly distributed over the whole surface and the absorption intensities do not correspond to those measured in solution.

The indicator properties of the sensitive membranes were almost the same as those of the free dyes, but the deprotonation occurred under more basic conditions. This is obviously due to the influence of the polymer, which function as a barrier to the ionic species and which also, with its hydroxyl group, causes additional stability of the acidic proton by hydrogen bond–formation. Another reason could be the isomerisation to the hydrazone–form during the polarity change of the composites with absorption of aqueous alkali solutions. In Figure 3–28 are shown the UV/vis spectra of covalent bound β–hydroxynaphthyl azo dye **51**.

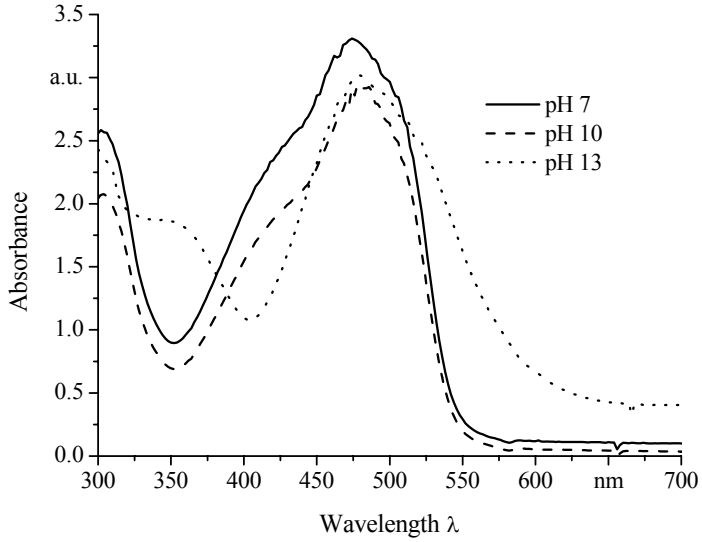


Figure 3–28: UV/vis spectra of composite **51** at different pHs

The deprotonation was shifted at pHs higher than 10, and the process was characterised by a shoulder from hydrazone form at 560 nm. The absorption of the hypsochromic hydroxyazo form could not be observed, and the functionality, which can be deprotonated exclusively, is the NH–group. This unsatisfactory colour change was also reported by Mohr *et al.*[45] Almost

the same behaviour was observed by the o–α–naphthol–azo dye–polymer conjugate **53** (Fig. 3–29):

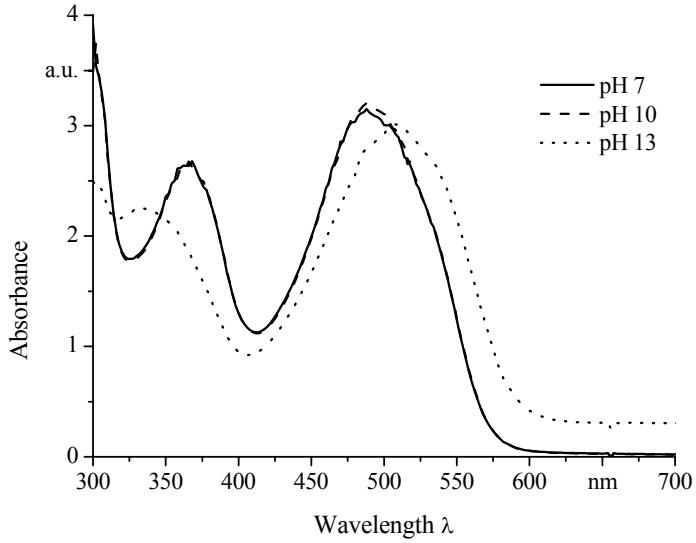


Figure 3–29: UV/vis spectra of composite **53** at different pHs

The dye exists only as the hydrazone–tautomer in the polymer matrix and deprotonation causes a bathochromic shift of the absorption maxima from 488 nm to 510 nm. This result is superior to the one obtained for composite **51**, because here the increase in pH is characterised by a shift of the absorption maximum, not just with a new shoulder. However, the measured difference of 22 nm between protonated and deprotonated form in composite **53** is too small to be used for fibre-optical detection. In both sensors deprotonation causes loss of coplanarity of the indicator dye–molecule, which is achieved by the intramolecular hydrogen bond. The possible rotations around the single N–N bond impair the conjugation of the π–system. As a result, the colour change is not pronounced, and the bands of the protonated and deprotonated form overlapp.

Composite **52** consists of a 1–phenylazo–4–naphthol–derivative linked to the PVA *co*–PE. The UV/vis spectra of its membrane at different pH buffers are shown in Figure 3–30:

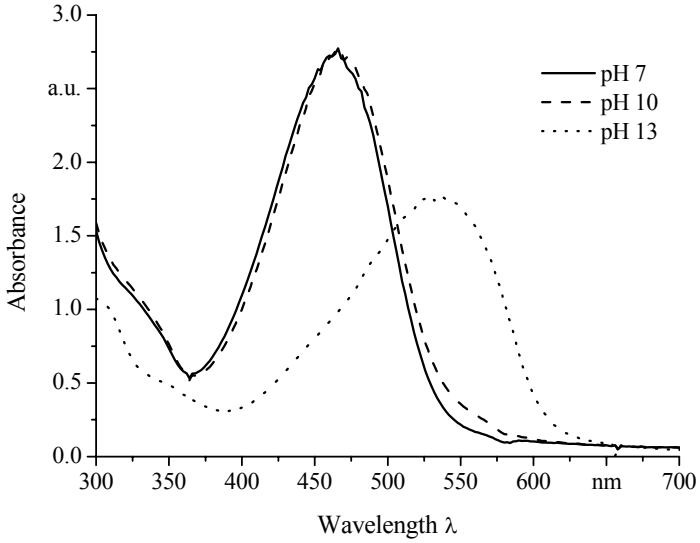


Figure 3–30: UV/vis spectra of composite **52** at different pHs

The indicator dye in the polymer matrix is in its hydrazone–form and during the deprotonation the coplanarity of the molecule is maintained. This causes a large bathochromic shift of the absorption maximum by 70 nm - from 463 nm to 533 nm. The absorption band is very broad, which is due to the fast equilibrium of the system, where pH 13 is not strong enough to deprotonate all indicator molecules. The colour change is extended to higher pHs as in the case of the previously described pH–sensors.

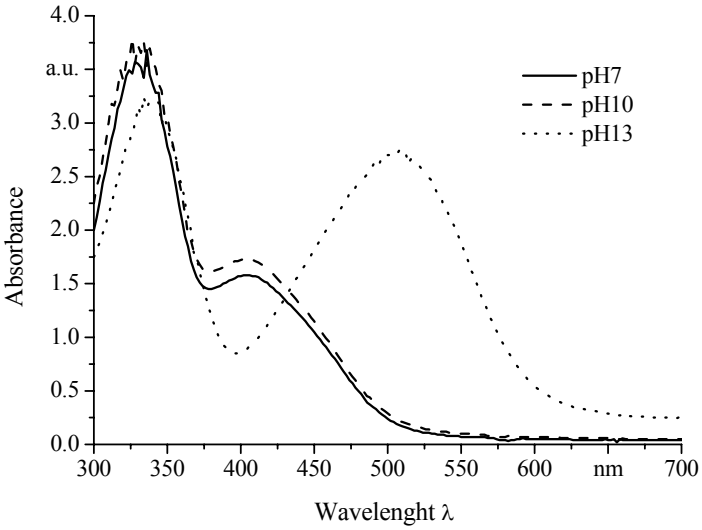


Figure 3–31**:** UV/vis spectra of polymer bound phenol azo dye **50** at different pHs

The best results were obtained with *p*–cresol azo dye–polymer **50**. The absorption spectra of the composite (Fig. 3–31), recorded of different pHs, showed the largest shift with respect to the thoses observed for the free dye.

The pH–dependency is shifted by more than 2 units with respect to the free dye. This can be due to difficulties of deprotonation, considering possible hydrogen bond formation between the hydroxyl groups of the poly(vinyl alcohol) and the dye. Another possibility consists in the direct transformation to the hydrazono–tautomer and consequently the need of higher pH for deprotonation. The difference between both protonated (402 nm) and deprotonated (506 nm) forms is the largest one - 104 nm, providing the possibility for exact pH-determination of the surrounding environment.

On the other hand there was not observed a change of the absorption maximum with every pH, as was the case for the free dye. Probably the diminished mobility of the dye within the polymer matrix allows that process to occur only at higher pHs.

These covalently bound dye–polymer composites are convenient for preparing films with excellent quality, flexibility and transparency, and they are suitable for fibre-optic measurements. The results of fibre-optical measurements with composite **50** are given in the next figure (Fig. 3–32).

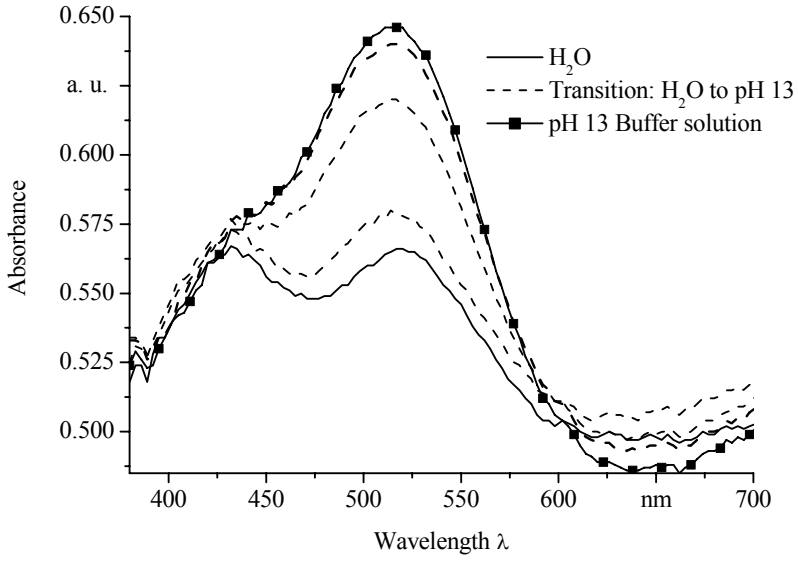


Figure 3–32: Fibre-optical UV/vis measurements of the pH using composite **50**

Figure 3–32 shows, that the pH–indicator dye in the sensor layer exists as an equilibrium of hydroxyazo and hydrazone tautomers, which are represented by absorption maxima at

430 nm and 517 nm, respectively. Both maxima are bathochromically shifted in comparison with the free dye (396 nm and 498 nm) and the membrane from the composite **50** (402 nm and 506 nm). This solvatochromism can be explained by the higher influence of the ionic strength of the surrounding environment.

Another interesting property is presented by the transition range from neutral media to pH 13. The disappearance of the low–wavelength maximum at 432 nm is not observed and only hyperchromic changes at 517 nm characterise the deprotonation of the dye. This offers the advantage to use the first maximum as internal reference by determination with only one sensor of the pH of the environment.

The response–time and reversibility of the sensor are demonstrated in Figure 3–33:

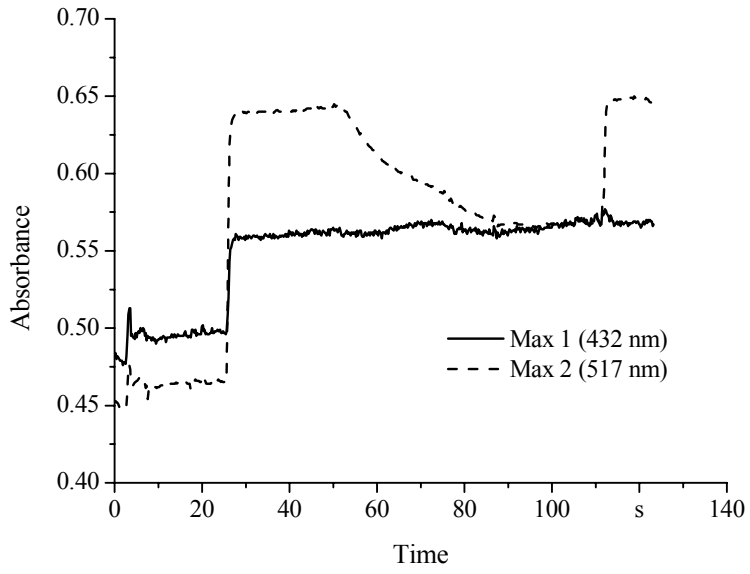


Figure 3–33: Response time and reversibility of the pH–indicator **50**

Approximately 20 seconds are necessary for the indicator layer to absorb certain amounts of water and to become more hydrophilic. The probe was placed in pH 13–buffer solution after 20 seconds. Then the low–wavelength maximum at 432 nm increased hyperchromically by 10 % and remained unchanged. The bathochromically shifted maximum at 517 nm undergo a drastic increase of almost 50 %. The response time of this process is only 2.3 sec, as shown in Figure 3–33. The reverse protonation, due to change of the pH 13–buffer solution to distilled water, was completed within 35 seconds. During that time the long–wavelength maximum decayed continuously to the same level of the first one. The reproductivity of the fibre-optical sensor sequal was demonstrated after minutes, when the probe was exposed again for the pH 13 buffer solution. The signal then changes within 2 seconds to the same level as observed

the previously. These fast sensor response times are observed only for the surface–tethered indicator dyes and superior to all other solid sensors. The described pH–indicator sensors consist of an indicator dyes, covalent linked to the polymer, which make them very durable and reliable. Moreover, the acetal as the spacer is extremely stable under the investigated conditions. Thus, no leaching or bleaching during long periods of time can occur. Another advantage is that the dye is homogeneously distributed over the whole volume of the polymer composite. Consequently, the sensor material is independent of other carriers, for example polyester or glass surfaces. It can be dissolved and used to cover micro–surfaces with different geometry by simple evaporation of the solvent. The sensitive areas possess high transparency and flexibility. All these factors allow the use of optical sensors for *in situ* monitoring of pH in concrete structures.

3.3.3. Optical properties of chloride–sensitive dyes

3.3.3.1. Optical properties of a complex–forming azo dye

As mentioned above (section 3.2.3), benzimidazole azo dye **122** is capable to form complexes with polar molecules. At alkaline pHs the ionic strength is assumed to provide an additional influence to the change of the tautomeric forms from azo to hydrazone. In Figures 3–34–36 are given the complexation behaviour of dye **122** at different pHs (10, 12 and 13).

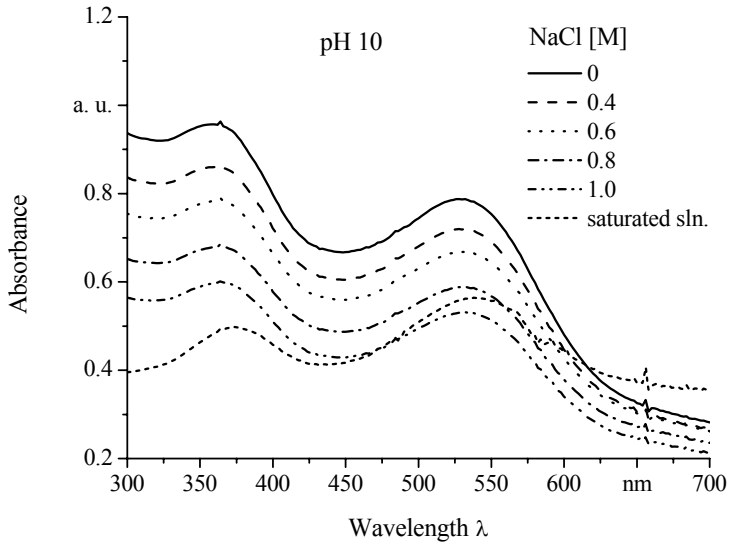


Figure 3–34: UV/vis spectra of dye **122** at pH 10 and different chloride concentrations

It was observed that at almost constant pH an increase of salt concentration led to hypochromic behaviour of both maxima, but more pronounced for the short–wavelength band at 365 nm. In all cases the short-wavelength maximum has the higher intensity. In saturated NaCl solution this caused precipitation of the dye, but **122** absorbed more intensive at 530 than at 365 nm.

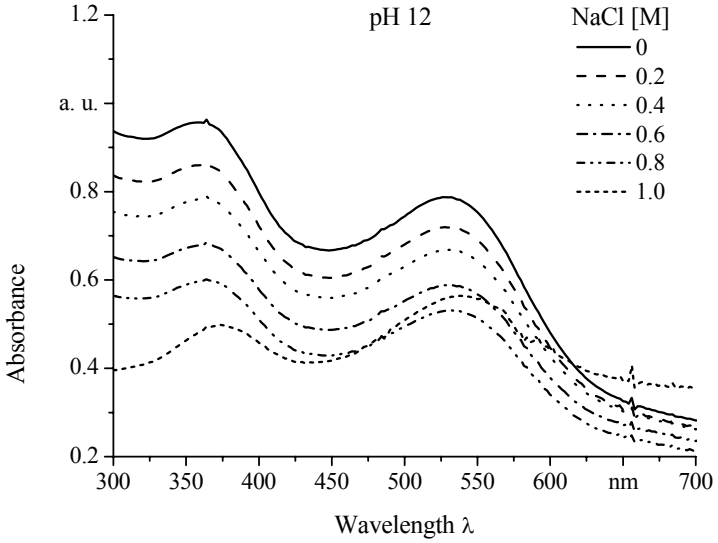


Figure 3–35: UV/vis spectra of dye **122** at pH 12 and different chloride concentrations

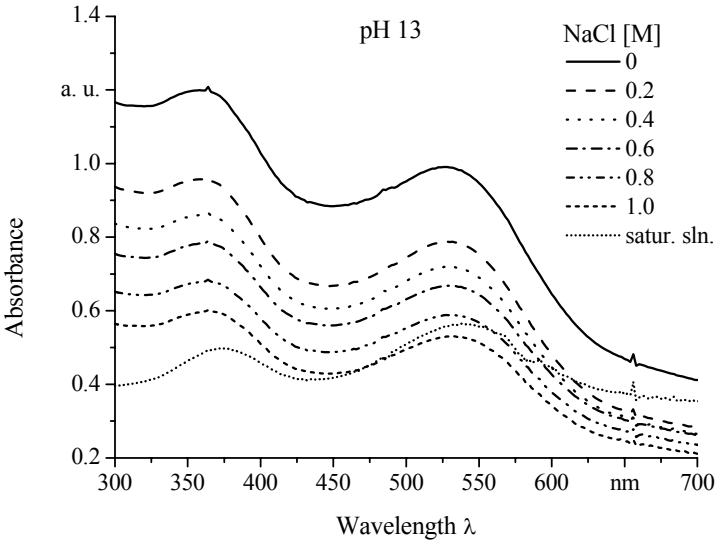
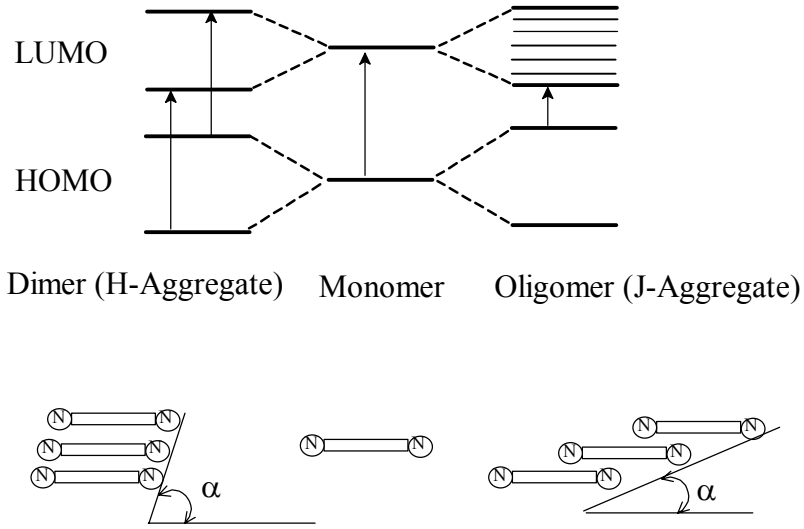


Figure 3–36: UV/vis spectra of dye **122** at pH 13 and different chloride concentrations

That dependance is the same over the whole alkaline region. Unfortunately, it is not selective for chloride anions only (Fig. 3–17) and the ionic strength also contributes significantly to the signals, as can be concluded from Figures 3–34–36. The quantification of the received signals is polynomial and different at any pH. These disadvantages cannot be compensated by the very good stability and the complete reversibility of dye **122** and it hence did not find an application in sensor preparation so far.

3.3.3.2. Aggregation of the polymethine dyes

The aggregation phenomenon of polymethine dyes and the explanation of the properties of these supramolecular structures are the topic of thousands of publications. The generally accepted model is based on the splitting (Davidov split) of the highest occupied molecular orbital - HOMO and lowest unoccupied molecular orbital - LUMO with respect to the 1–D stack–order in the aggregates:



Scheme 3–36: Model of energy splitting of the frontier MOs (HOMO–LUMO) in the molecule, their orientation in the 1–D stack with regard to the slip angle α

The H–aggregate splitting of the HOMO and LUMO causes on increase of the energy barrier, resulting in a hypsochromic shift of the absorption spectra. This could be due to the attraction between the counter–charged dipoles in the dye molecule. This can induce a decrease of the relative power of the donating part as well as the electron–withdrawing capability of the acceptor part in the chromophore chain caused by the neighbouring molecule. Consequently, the system will show a decrease in energy, respectively, an increase of the charge–transfer within the molecule.

The early Scheibe theory has explained the H-aggregates as increasing excitation from the top of the HOMO to the top of the– LUMO band. However, according to Tyutyulkov this can be explained also by a transition from the bottom of the LUMO –band to the bottom to the HOMO –band.[136] Another important characteristic of the aggregates is the slip angle α. It is

defined as the angle between the long molecular axis and the translation axis of the stacks. For H–aggregates that angle is $\alpha = 50°$ to 90° and almost full face–to–face configuration in the 1–D stack.

The bathochromically shifted *J*–absorption band, with respect to the monomer, is caused by the excitation from the top of the LUMO level to the bottom of the HOMO. The energy decrease of that transition can be explained with increased interaction between the dye molecules caused by a small tilt angle α, which has values ranging from 30 to 55°. The result is the red–shifted, narrow band of the *J*–aggregates.

There is no clear answer how the chloride ions force the polymethine molecules to form *J*–aggregates. Schaberle *et al.* proposed a reduction of repulsion between the dye molecules, due to formation of an atmosphere of chloride ions around them.[137] This should reduce the dye effective charge and thus stimulate aggregation at lower concentrations. On the other hand the Cl^- atmosphere could disturb the formation of face–to–face stacks sterically and H–aggregates respectively and in this manner favour face–to–tail (*J*) aggregation.

The absorption spectra of the benzimidazolecarbocyanine dyes **104**, **105**, **106** and **107** were recorded in different solvents in order to investigate the influence of highly alkaline pHs and different chloride ion concentration upon *J*–aggregates formation. For a better evaluation of their properties, the absorption was measured in different solvent mixtures in order to find conditions, were both M– and *J*–forms are available.

3.3.3.3. Aggregation behaviour in different solvents

In pure organic solvents (DMSO, DMF, EtOH) trimethine dyes **104**, **105**, **106** and **107** show only M–bands in their UV/vis–absorption spectra. The absorption maxima and molar extinction coefficients are given in Table 3–11:

Table 3–11: Absorption maxima and molar extinction coefficients of synthesised trimethine dyes in different solvents.

Dye	EtOH		DMF		DMSO	
	λ_{max}, [nm]	ε, [l·mol^{-1}·cm^{-1}]	λ_{max}, [nm]	ε, [l·mol^{-1}·cm^{-1}]	λ_{max}, [nm]	ε, [l·mol^{-1}·cm^{-1}]
104	526	123 000	522	118 000	528	137 000
105	526	202 000	520	152 000	528	164 000
107	542	55 000	536	63 000	544	47 000
106	528	182 000	522	130 000	530	183 000

Typically, tetrabromo trimethine **106** gave higher molar absorption coefficients than the tetrachloro–derivative **104** in all solvents, presumably caused by the bulky bromine atoms in 5,5',6,6'–position. Their volumes are exceeded only by cyanine **105** in EtOH and DMF, due to the longer *N*–alkyl chain.

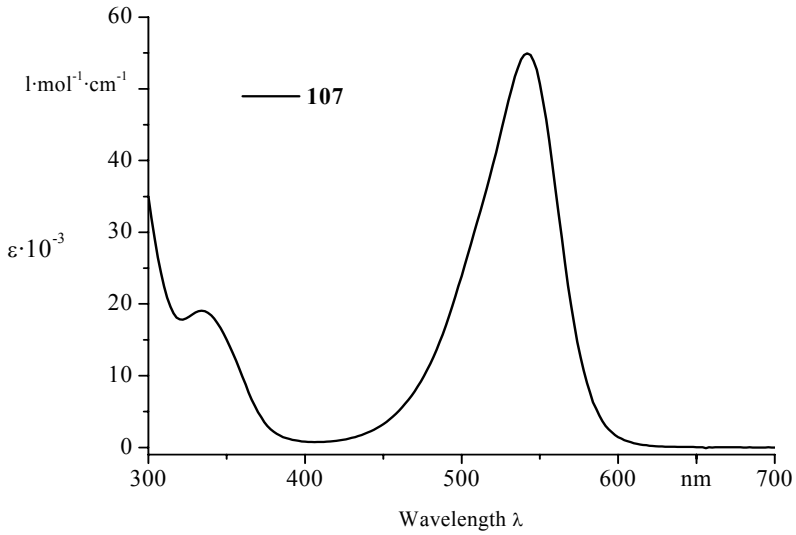


Figure 3–37:UV/vis spectra of **107** in DMF, conc. 1.7·10^{-5} M

The *meso*–phenyl–substituted dye **107** shows a very broad absorption band (Fig. 3–37). It can be assumed as the M–band in accordance with its absorption maximum and its bathochromic shifts by 10 to 20 nm with respect to the *meso*–unsubstituted trimethines **104**, **105** and **106**. That shift is caused by the phenyl ring, which can be assumed as a conjugative extension of the chromophor chain.

Its low intensity is not typical for such dyes and, in addition, the colour of the solution in different solvents seems to be very similar to those of *J*–aggregates formed by the dyes **104**, **105** and **106**. The configuration of the dye is neither identical with the monomer, nor with the *J*–states. These structures are known as "poly–molecular associates".[138] An example, **107**, showed no bathochromic (*J*) or hypsochromic (H or D) bands in different solvents or in the presence of any ionic species.

Different solvent mixtures were investigated, in which *J*–aggregation can be assumed to exist. No *J*–aggregation can be observed for dye **105** in solutions containing more than 30 % (v/v) organic solvents. The absorption spectra of **105** and **106** in different aqueous organic solvents are shown in Figure 3–38:

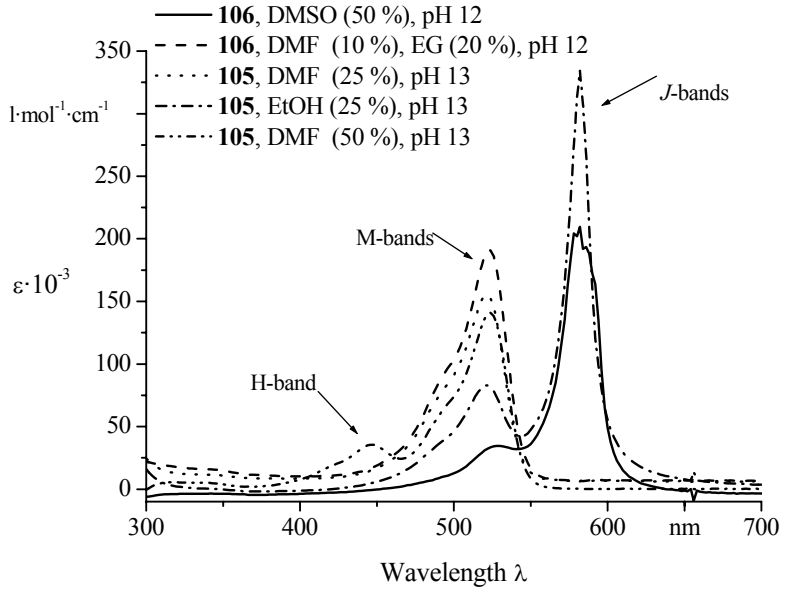


Figure 3–38: pH–dependent UV/vis absorption spectra of cyanines **105** and **106** in aqueous solutions (v/v) of different organic solvents. Concentrations: **106**, DMSO (50 %, pH 12)– $1.2 \cdot 10^{-5}$ M ; **106**, DMF (10 %), EG (20 %), pH 12–$4.8 \cdot 10^{-6}$ M ; **105**, (DMF 25 %, pH 12)–$5.2 \cdot 10^{-6}$ M ; **105**, (EtOH 25 %, pH 12)– $5.2 \cdot 10^{-6}$ M ; **105** (DMF 50 %, pH 13)– $5.6 \cdot 10^{-6}$ M

No *J*–band was observed for **105** in DMF (50 %) at pH 13, but distinct H–bands are formed with maxima at 446 nm. In contrast, aggregation plays a considerable role for this dye in EtOH (25 %) at pH 13 and it is indicated by the band with a peak at 586 nm. At pH 12, no *J*– and H–band formation are observed in any aqueous organic solvents. **106** displays predominantly *J*–band formation in DMSO (50 %) at pH 12, whereas in DMF (10 %, with 20 % EG) only the pure monomer form is present. Obviously, protic polar solvents such as EtOH and EG favour the formation of aggregate structures in organic–aqueous solutions. Probably, they form a surrounding intermolecular layer by hydrogen bonds with the water and solvated salts, facilitating the interaction between the dye molecule and the solution. In order to avoid the fast saturation of the aggregates in solution the last aliquot (10 % with 20 % EG, v/v) was used. That solvent mixture guarantees the equilibrium between M and *J*–states and avoids the saturation. The use of similar solvent compositions has been reported by Berlepsch *et al.*[40 b]

3.3.3.4. Chloride sensitivity

The sensitivity of the trimethine dyes towards chloride was investigated in alkaline solutions to simulate the real conditions in reinforced concrete.

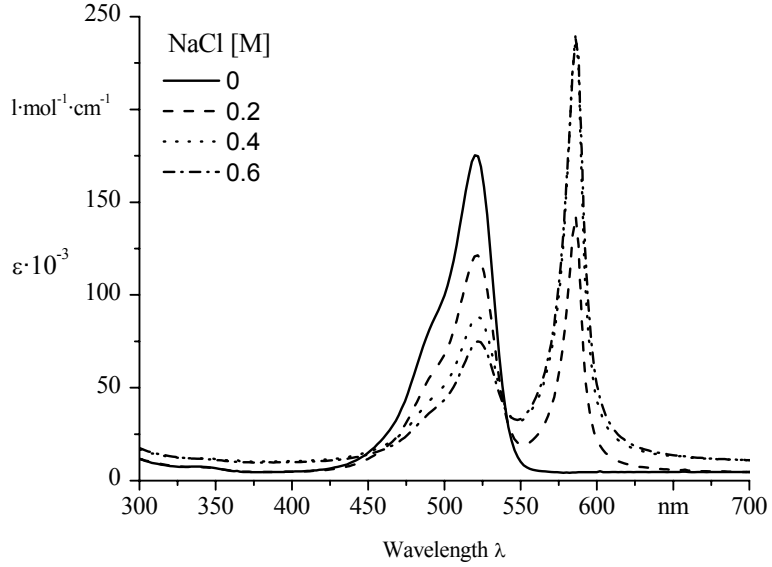


Figure 3–39: Chloride dependence of the absorption spectra of dye **105** in DMF 10 %, 20 % EG at pH 12, conc. - $5.4 \cdot 10^{-6}$ M.

The absorption spectra of dyes **104**, **105** and **106** show considerable chloride dependencies in the range from C_{Cl^-} = 0.0 to 0.6 M in DMF (10 % with 20 % EG) at pH 12 and 13 (Figures 3–39–44). In Figures 3–42 and 3–43 are shown the *J*–aggregation of **105** upon addition of NaCl at pH 12 and 13. In the first case a clear dependence on salt concentration was observed: The intensity of the monomer band (λ_{max} = 522 nm) decreased continuously, whereas the intensity of the *J*–band (λ_{max} = 584 nm) increased. Though the monomeric as well as the aggregated forms are present at any of these chloride ion concentrations, some saturation of aggregate structure can be assumed for chloride concentration > 0.4 M (Fig. 3–39).

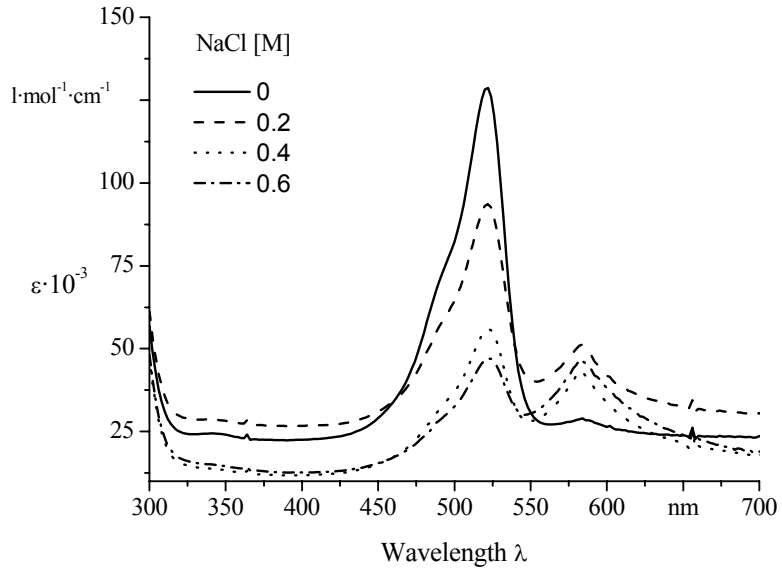


Figure 3–40: Chloride dependence of the absorption spectra of dye **105** in DMF 10 %, 20 % EG at pH 13, conc. $5.4 \cdot 10^{-6}$ M.

This assumption is supported by measurements at pH 13 (Fig. 3–40); even in the absence of chloride ions a small amount of *J*–structures was detected. Addition of NaCl caused an increase of the *J*–bands, which become saturated with increasing chloride concentration (> 0.2 M). This is in accordance with De Rossi *et al*,[40a] who investigated *J*–aggregation as a function of the length of the *N*–alkyl chains of cyanine dyes.

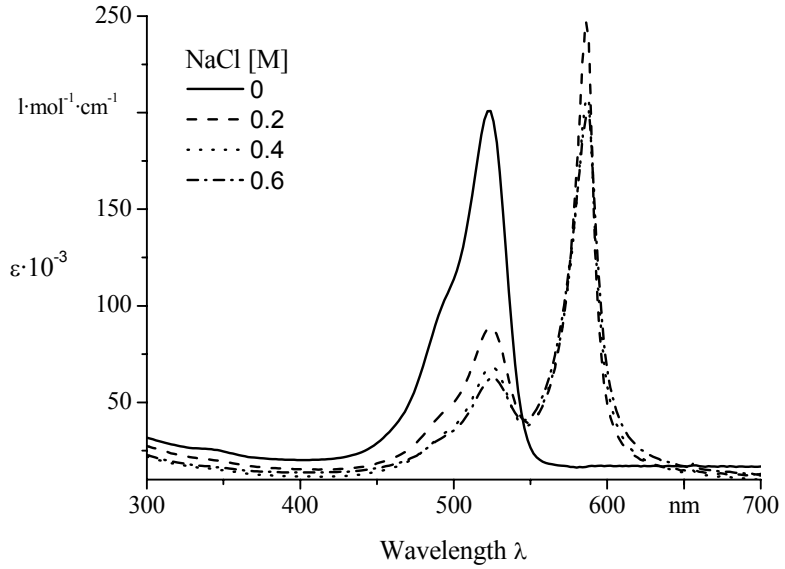


Figure 3–41: Chloride dependence of the absorption spectra of dye **106** in DMF 10 %, 20 % EG at pH 12, conc. $4.8 \cdot 10^{-6}$ M.

The influence of the bulky substituents in the 5 and 6–positions of the benzimidazolic end groups - the four bromine atoms - was examined with dye **106**. As mentioned above, the tetrabromotrimethine exhibits a strong tendency to aggregate, even in media consisting of 50 % organic solvent at pH 12 (Fig. 3–38).

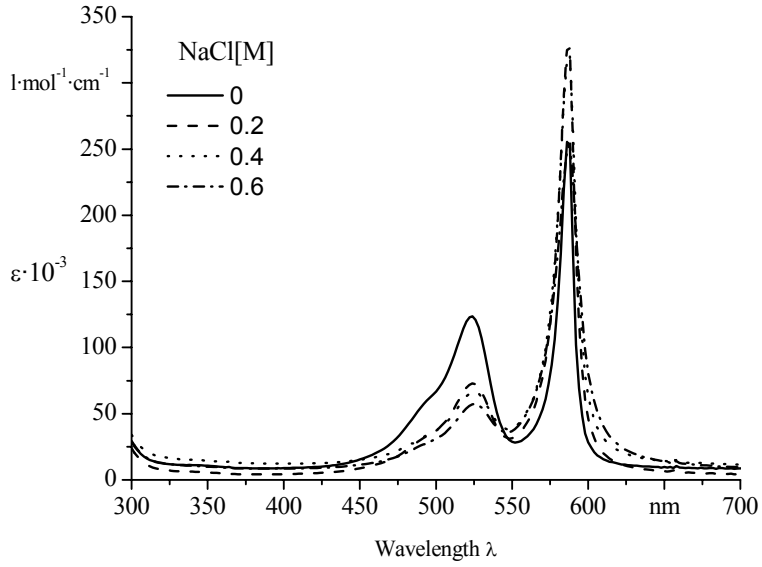


Figure 3–42: Chloride dependence of the absorption spectra of dye **106** in DMF 10 %, 20 % EG at pH 13, conc. $4.8 \cdot 10^{-6}$ M.

At pH 12 the aggregate structures are present even at low salt contents to a marked extent. Increase of the chloride concentration leads to saturation of the *J*–band, while the monomer–band decreases. At pH 13 the formation of these supramolecular forms becomes more important. This form is present already in the absence of salt. Similar to the situation at pH 12 saturation of the *J*–band appears at C_{Cl^-} = 0.2 M and further addition of NaCl leads only to a small decrease of the M–bands.

Very interesting spectra were observed for cyanine dye **104** (Fig. 3–43 and 3–44): The chloride dependence of the relative intensities of the *J*– and M–bands is pH independent in these cases.

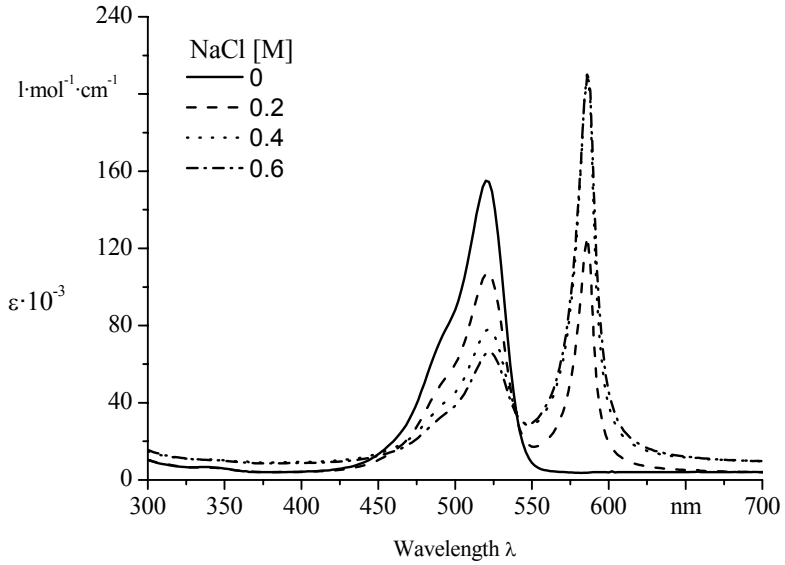


Figure 3–43: Chloride dependence of the absorption spectra of dye **104** in DMF 10 %, 20 % EG at pH 12, conc. $5.6 \cdot 10^{-6}$ M.

Any addition of NaCl leads to a considerable decrease of the M–bands and, respectively, marked increase of the *J*–bands, respectively. The effect of saturation of aggregates is observed only for extremely high salt concentrations ($C_{Cl^-} > 0.6$ M). This absorption behaviour turns out to be most promising for the use as a sensor material.

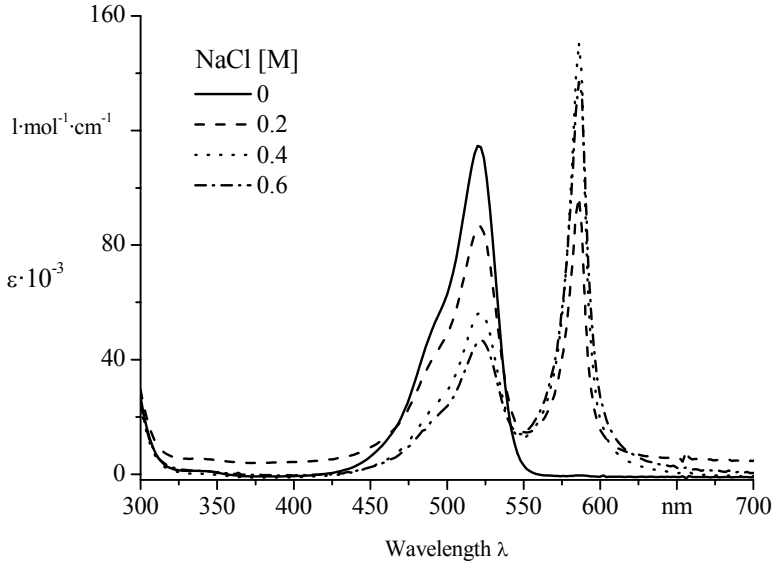


Figure 3–44: Chloride dependence of the absorption spectra of dye **104** in DMF 10 %, 20 % EG at pH 13, conc. $5.6 \cdot 10^{-6}$ M.

Since both M– and *J*–states are present in solution, the relative intensity of their absorption bands can hence be applied for quantitative determinations. For this reason the specific ε–value of each form was correlated with the chloride ion concentration (Fig. 3–45 and 3–46):

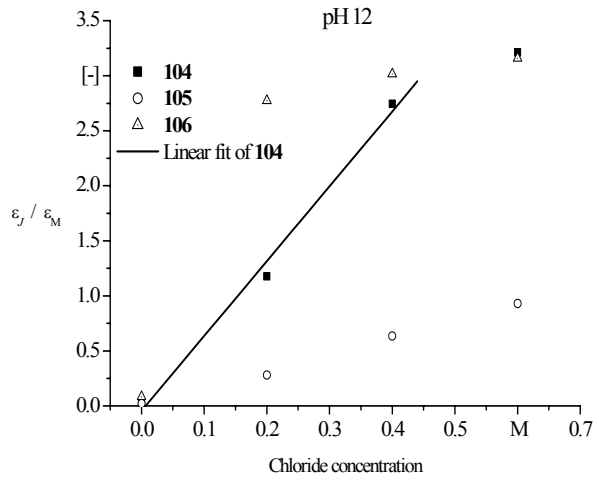


Figure 3–45: Correlation of $\varepsilon_J/\varepsilon_M$ at pH 12 with chloride ion concentration for dyes **104**, **105** and **106**

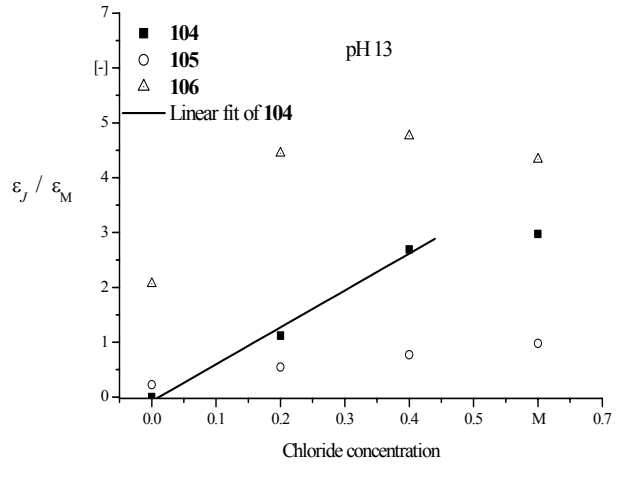


Figure 3–46: Correlation of $\varepsilon_J/\varepsilon_M$ at pH 13 with chloride ion concentration for dyes **104**, **105** and **106**

As can be seen from the last two figures, only dye **104** exhibits an almost linear dependence at both pHs at concentration of chloride ions up to 0.4 M which renders the determination of chloride concentrations possible.
For all other dyes a higher order polynomial dependence is observed, reflecting the saturation effect even at low and middle chloride ion concentrations ($C_{Cl^-} > 0.4$ M).

3.3.3.5. Chloride dependence and selectivity of sensitive membrane

In principle, three types of sensor matrixes can be considered depending on their physical-chemical properties: solutions, gels and polymers. The solutions are employed to a great extent in "classical" analytical chemistry. They are prepared very easily, show sufficient transparency with respect to UV/vis–spectrometric investigations and exhibit extremely short response times. However, their practical application is slargely limited to laboratory use.
Gel–structures combine beneficial properties of both polymer and solution. They are capable to absorb large amounts of solvents, with $M_{solvent}/M_{gel} >> 1$ in many cases. Their use as sensor matrices for optical detection have been reported.[34, 139]
Our initial approach also included gel preparation as an intermediate step. Seitz *et al*. have reported the application of PVA (cross–linked with glutaraldehyde) for the preparation of optodes.[140] Benzimidazolocarbocyanine **104** was assumed to form *J*–aggregates within such gels. Unfortunately, these sensor matrices turned out to be quite unstable with respect to their optical transparency and mechanical durability. Alternatively, poly(vinyl acetals) with a sufficient degree of acetalisation were developed in order to avoid water solubility and to remain optical transparent in the investigated environment as well as to enable possible *J*–aggregation of the embedded trimethine dyes. The result of the absorption measurement obtained with acetals (degree of acetalisation with butyraldehyde > 40 %) resembled that of the solution experiments: no *J*–aggregation was observed due to the low content of water within the polymer.
The capability of the polymer to absorb water depends strongly on the content of free hydroxyl groups, which form hydrogen bonds with the water molecules. The results of UV/vis absorption measurements of PVA (degree of acetalisation: approximately 30 %) doped with the dye **104** are shown in Figure 3–47:

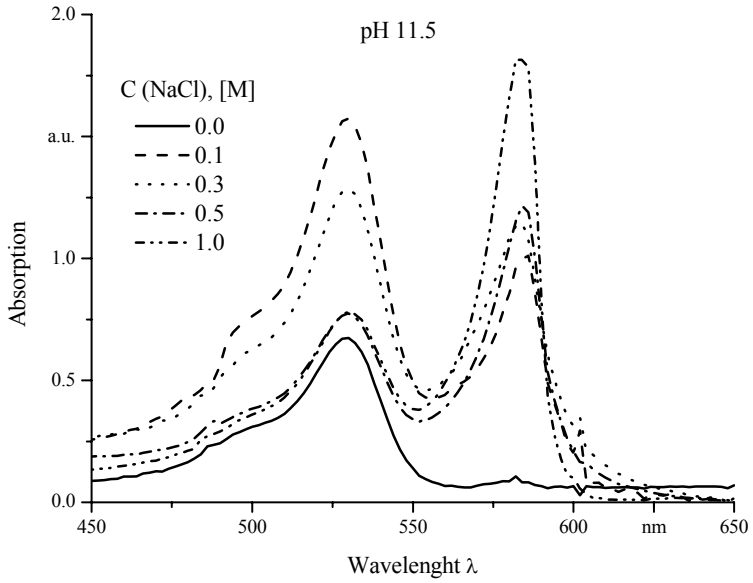


Figure 3–47: Vis absorption spectra of a polymer membrane doped with dye **104** (host–guest system, PVA *co*–PVB (app. 30 mol %) 24 h after preparation.

As can be seen, formation of *J*–aggregates of **104** takes place in the polymer film composed from PVA *co*–PVB. Similar to the results obtained in different aqueous solvent systems (Fig. 3–43 and 3–44), the aggregation process within the polymer depends strongly on the concentration of chloride ions.

In addition, the *J*–state within the polymeric environment turns out to be more sensitive to the pH as in solution. A small amount of aggregates is also observed in the absence of chloride ions. This influence to the sensor can be eliminated with the help of a calibration curve and is therefore not assumed to cause significant experimental error.

We have tested our sensor also for selectivity towards other anions, which are present in reinforced concrete.

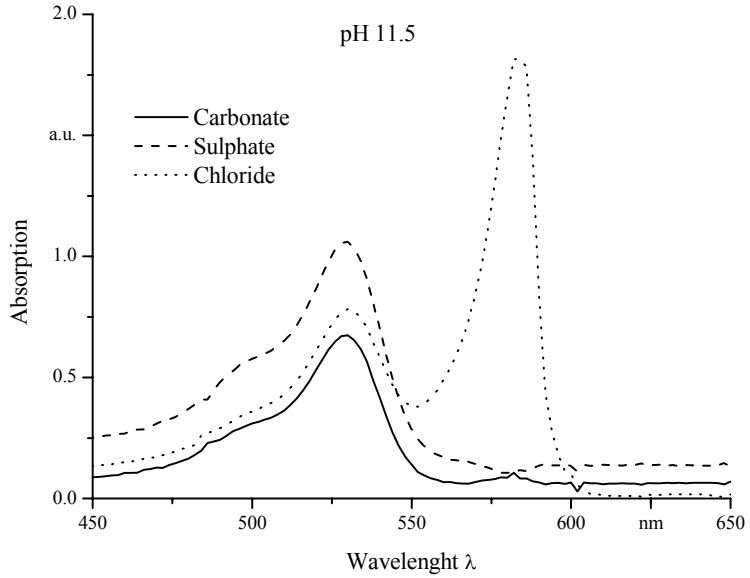


Figure 3–48: Selectivity of the sensor membrane doped with dye **104** (host–guest–system, PVA *co*–PVB (app. 30 mol %) 24 hours after preparation versus carbonate and sulfate anions.

As shown in Figure 3–48, no *J*–formation is induced by carbonate and sulphate ions. The weak *J*–band observed in the presence of carbonate is assumed to be rather pH–dependent, *i.e.* caused by the strongly alkaline environment.

The 5,6,5′,6′–tetrachalogenosubstituted 2,2′–benzimidazolocarbocyanines presented here are promising materials for application in the optical determination of the concentration of chloride ions under strongly alkaline conditions. Within the absorption spectra of these dyes the M–bands loose in intensity with increasing chloride concentration, whereas the bands caused by *J*–aggregates essentially increase. The relative intensities of the maxima of the M– and *J*–band ($\varepsilon_M / \varepsilon_J$) can almost be linearly correlated with chloride ion concentration. This correlation is nearly pH independent for 1,1′–dibutyl–5,6,5′,6′–tetrachloro–3,3′–bis–(4–sulfobutyl)–benzimidazolotrimethine **104** in an alkaline aqueous organic solvent (DMF 10 %, 20 % EG). A suitable polymer - poly (vinyl alcohol *co* approximately 30 mol % vinyl butyral) was developed, in which *J*–aggregates of the doped dye **104** are formed. The composite was tested successfully for selective determination of chloride in the presence of sulphate and carbonate ions. To the best of our knowledge, this is the first method for optical determination of chloride ions under strongly alkaline conditions. It is of potential interest for the preparation of sensor systems for fibre-optical *in situ* monitoring of chloride ion in reinforced concrete.

4. Summary

In this work indicator materials were developed for *in situ* monitoring of corrosion processes in reinforced concrete. These materials are composed of indicator dyes, which are incorporated into suitable polymers by covalent bonding (pH–indicators) and as host–guest systems (chloride sensors).

Nearly fifty new compounds – dyes and precursors and eight dye-polymer composites, which were not found in the literature, have been synthesised, identified and investigated for practical use in this dissertation. In the first part of the study a new class of reactive pH–indicator azo dyes was synthesised and characterised. Aliphatic aldehydes were used as reactive intermediates for the first time and resulted in formation of acetals as a "double connection" to the polymers. The aldehyde group was introduced with two kinds of spacer links - alkylsulphone and sulphonamide.

The synthesis of the appropriate alkylsulphones was performed by photochemical radical addition of 1,3-dioxolane to the vinylsulphone group. This resulted in elongation by one carbon atom of the alkyl chain and introduction of protected aldehyde group in the diazo consisting part of the azo dyes. Two synthetic routes were developed - the dioxolane was joined to the vinylsulphonyl azo dyes and to the corresponding vinylsulphonylaniline. The reactions with dyes occur in low yields for the *p*–cresol dye **18** and failed completely with naphthol derivative **21**, probably because of ketohydrazone tautomerism. An attempt with the precursor of these dyes, the aniline **23**, took place in quantitative yield, and only 5–10 min were required for completion of the reaction. The prepared dioxolanylaniline were successfully diazotised and coupled with various phenols and naphthols. The protective group was consequently removed to obtain the aldehyde group.

Another opportunity for connecting unit was provided by the sulphonamide group. In these cases the amine, bearing the protected aldehyde group as acyclic acetal, reacted with nitroarylsulphonyl chloride. The prepared acetal aniline was unstable to diazotisation. The conversion to the cyclic acetal as protective group resulted in the formation of sulphonamide acetal dyes in good yield.

The reactive azo dyes can be represented by the following general formula,

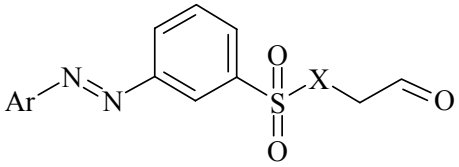


Figure 4–1: General formula of the synthesised reactive azo dyes

where X is methylene or amidomethylene and Ar - *p*–cresol, α– or β–naphthol. The *m*–position of the sulphone acceptor was preferred because of weak conjugation to the hydroxyl group and, consequently, resulted in dyes, which are weak acids. Hence, highly pHs will be required to deprotonate the indicator azo dyes. This allows a shift of their colour change to the pH–range from 9 to 13.

All dyes were successfully linked to the vinylalcohol units in poly(vinyl alcohol *co*–ethylen) polymer *via* an 1,3–dioxane connecting group. The dioxane ring was formed by the reaction of the reactive aldehyde group of the dyes with the 1,3–diol moieties of two vinylalcohol units from the copolymer. This type of covalent bonding is assumed to be stable for a long period of time under basic conditions and does not affect the optical determination of the absorption changes of the dyes. Such pH–sensors show short response times and the color changes are completely reversible. They can be joined to the optical fibres and are promising candidates for a long term precise monitoring of the pH of reinforced concrete.

To cover the whole alkaline pH range, two anthraquinone monophenyl hydrazone dyes were synthesised (Fig 4-2).

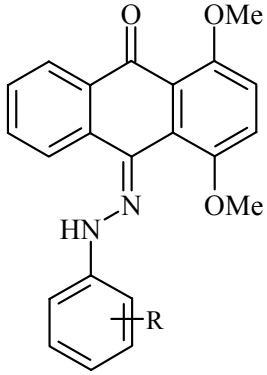


Figure 4-2: Structure of synthesised anthraquinone monophenyl hydrazone

Their colour changes occur beyond pH 13. Based on these properties they can be modified and also covalently bond to the polymers to create pH sensors for an extremely high alkaline environment.

In the second part of this work optical sensors for the determination of chloride ion in alkaline media were developed. Three different methods were investigated - selective fluorescence quenching of acridone and acridine derivatives (Fig.4-3), complex formation with benzimidazole azo dyes (Fig. 4-4) and *J*–aggregation of bisbenzimidazole trimethines (Fig.4-5).

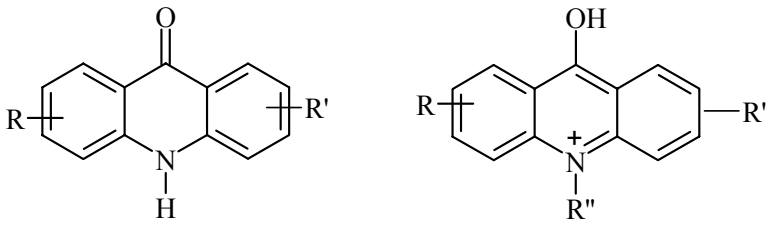


Figure 4-3: Structure of synthesised acridone and acridine derivatives

The first approach with electron rich acridones and acridines was unsuccessful, no quenching of the fluorescence signal being observed. The attempted quatenisation of the nitrogen atom by a functionalised acridine molecule also failed.

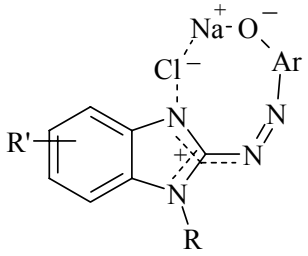


Figure 4-4: Structure of synthesised complex-formation azo dye

The benzimidazole azo dye **122** was capable to form complexes with chloride ions, but there was a pronounced influence of the basicity of the environment, and the dye tended to form complexes with other anions and polar molecules. A single crystal X–ray structure supported this behavior: the dye formed a complex with EtOH, which was used as the solvent for crystal growth.

The last opportunity gave very good results. The synthesised tetrachloro bisbenzimidazole trimethine dyes **104** form *J*–aggregate under the influence of chloride ion. Their structure is represented in Figure 4–5:

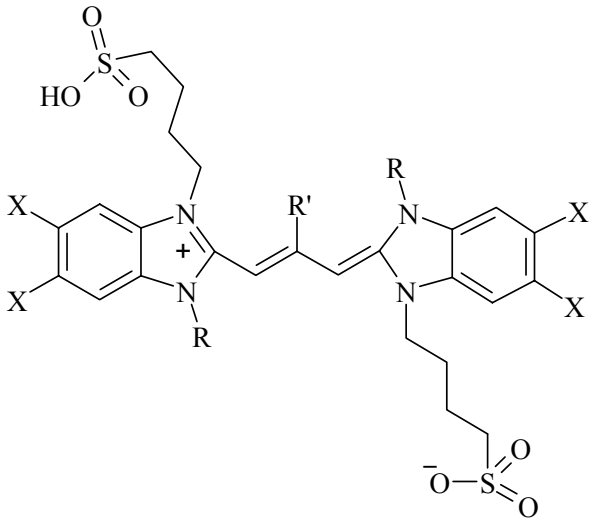


Figure 4–5: General structure of synthesised 1,1′–dialkyl–5,6,5′,6′–tetrahalogeno–3,3′–bis–(4–sulfobutyl) benzimidazolotrimethines, where X = Cl or Br, R = alkyl (C_4 or C_6) and R' = H or Phenyl

In the absorption spectra of these dyes the M–bands decrease in intensity with increasing chloride ion concentration, whereas the bands caused by *J*–aggregates increase significantly. The relative intensities of the maxima of the M– and *J*–band ($\varepsilon_M / \varepsilon_J$) are almost linearly correlated with the chloride concentration. This dependency is pH–independent for 1,1′–dibutyl–5,6,5′,6′– tetrachloro–3,3′–bis–(4–sulfobutyl)–benzimidazolotrimethine **104** in an alkaline aqueous organic solvent (DMF (10 %, with 20 % EG)). A suitable polymer–poly(vinyl alcohol *co*–app. 30 mol % vinyl butyral) was developed, in which *J*–aggregates of the doped dye **104** are formed. This polymer was tested successfully for selective determination of chloride in the presence of sulfate and carbonate. To the best of our knowledge, this is the first method for optical determination of chloride ions under strongly alkaline environment. It is a promising sensor system for fibre-optical determination of chloride ion concentration in reinforced concrete, and could make non–destructive *in–situ* monitoring of the corrosion in reinforced steel become a reality.

5. Experimental Section

5.1. General remarks

Thin layer chromatography (TLC):

Silica gel "Polygram SIL G/UV_{254}", Aluminium oxide "Polygram ALOX N/UV_{254}" and Silica gel reverse phase "Alugram ® RP–18W/UV_{254}" (Macherey–Nagel&Co.).

Preparative layer chromatography (PLC):

PLC–plates 20 × 20 cm Silica gel 60.2 mm (Merck Nr. 1.05745).

Flash chromatography (FC):

Silica gel "Kieselgel 60" (63–200 μm–Merck) or aluminium oxide "ICD Alumina N Super 1" (ICN Biomedicals GmbH). The ratio of stationary phase to mixture to be separated was ca. 100–120/1.

Melting points:

The melting points were determinated on "E. Leitz" hot stage microscope apparatus and are uncorrected.

IR spectroscopy:

IR spectra were recorded on a Nicolet 320 FT–IR spectrometer (apparatus 1–IR^1) and Bruker Tensor 27 using the "Diamond ATR" technique (apparatus 2–IR^2). Intensities of the bands are described as w (weak), m (medium), s (strong) and vs (very strong).

UV/vis spectroscopy:

UV/vis spectra were recorded on a "Hewlett Packard 8452 A" diode array spectrophotometer.

Mass–spectrmetry:

Mass spectra were obtained on a Finnigan MAT 8400–MSSI spectrometer, using either EI (Electron Impact, 70 eV), FAB (Fast Atom Bombardment) with 3–Nitrobenzylalkohol (NBA) as matrix and argon as ionic source (8 kV) or ESI (Electron Spray Injection).

NMR–spectroscopy:

The NMR spectra were recorded on a Bruker Avance GRX–400 spectrometer in $CDCl_3$, DMSO–d_6 and acetone–d_6 with frequencies of 400.13 MHz and 100.61 MHz, for ^1H and ^{13}C NMR, respectively. Routine NMRs were performed on a Bruker AC 200 spectrometer (^1H–200.13 MHz and ^{13}C–50.32 MHz). When not indicated, the measurement was performed with the first apparatus. Chemical shifts are reported in parts per million (δ) downfield from the

internal tetramethylsilane reference. The multiplicity of the signals is given as: s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), sx (sextet), m (multiplet), dd (doublet of doublets), ddd (doublet of doublets of doublets), td (triplet of doublets) etc.

X–ray structure determination:

The following diffractometers were used for the X–ray structure analyses: STADI–4; Bruker SMART 1000 CCD. The X–ray data were processed and refined with the SHELXL–97 programs.

The elemental analysis:

The analysis were carried out by the analytical laboratory of the Institute of Pharmaceutical Chemistry, Technical University of Braunschweig.

General conditions:

All commercial reagents were of analytical grade and were used as received. All solvents were purified by distillation before use and, when needed, dried by prescribed procedures. Photochemical reactions were carried out in a water–cooled 400 mL reactor with mercury low–pressure (10 W) and medium–pressure (150 W) lamps (Heraeus) inside. 1,3―dioxolane, which played the role of solvent and as well as reagent was freshly distilled and degassed by passage of argon for 15 min. The substances were dried at 0.1–0.2 mm Hg.

5.2. General procedures

5.2.1 Azo dyes

5.2.1.1. Diazotisation

The amine (10 mmol) was dissolved in 6 *N* HCl (25–30 mmol). The mixture was cooled by means of an ice–water bath and an aqueous solution of $NaNO_2$ (15 %, 7 mL) was added dropwise within 15 min. The resulting yellow to orange solution was stirred at that temperature for 1 h. Finally the excess of HNO_2 was destroyed by adding solid urea (0.50 g).

5.2.1.2. Azo Coupling

The thus prepared solution was added to a solution of the appropriate phenol (10 mmol) in aqueous NaOH solution (10 %, 15 mL) at 3–5 °C under vigorous stirring. After stirring for 40 min, the mixture was neutralised by adding 2 *N* HCl (20 mL). The precipitated dye was isolated by filtration and washed with water (3 × 50 mL). Purification was achieved by flash chromatography and recrystallisation using the solvents given below.

5.2.2 Introduction of the vinylsulphonyl group

The following procedure is an improvement of the method described in reference:[45b]
Concentrated sulphuric acid (20 mL) was added in small portions and under vigorous stirring to a solution of 2–(3–aminophenylsulphonyl) ethanol hydrochloride (5.00 mmol) at 25 °C under nitrogen. After stirring for 2 h the mixture was poured into ice water (100 mL) and neutralised by careful addition of solid Na_2CO_3. The temperature was kept at 15–20 °C by adding the appropriate amount of ice. After addition of diethyl ether (100 mL) aqueous NaOH (30 %, 20 mL) was added carefully. The organic phase was separated, and the aqueous phase was extracted with diethyl ether (3 × 50 mL). The combined ethereal solutions were

dried (Na_2SO_4) and the solvent was removed *in vacuo*. The crude product was purified by flash column chromatography.

5.2.3 Photochemical addition

A procedure for photochemical synthesis of acetals was used.[66] Benzophenone was used as a photochemical sensitiser in molar ratio 1:1 with respect to the vinylsulphonyl compound. The reaction was carried out under argon, under water-cooling and was complete in 5–60 min. Purification of the products was performed by flash chromatography.

5.2.4 Deprotection of the formyl group

To a solution of the acetal–protected dyes **18** and **39**–**41** and **31a** (2.0 mmol) in a mixture of acetone (30 %) in water (total volume: 30.0 mL) H_2SO_4 (15.0 %, 10.0 mL) was added, and the resulting mixture was refluxed for 3 h. Subsequently, water (200 mL) was added and the resulting precipitate was isolated by filtration and washed with water (2 × 50 mL). The filtrate was extracted with diethyl ether (3 × 30 mL) and the combined ethereal solutions were washed with aqueous $NaHCO_3$ solution (1.0 %, 50 mL). After drying (Na_2SO_4) the solvent was removed in a rotary evaporator. The aldehydes **19** and **44**–**47** were purified by flash chromatography.

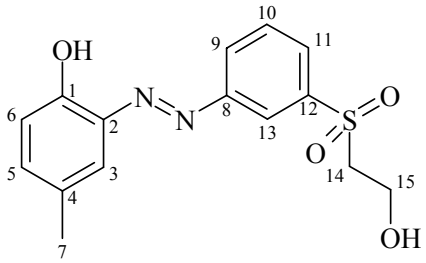
5.2.5 Covalent bonding of the dyes

Poly (vinyl alcohol *co*–ethylene) (500 mg, ethylene content: 27.0 %) was dissolved in DMF (30 mL) at 100 °C and the reactive dyes **19** and **44**–**47** (40 mg, 0.11–0.12 mmol) were added. After addition of conc. HCl (2.0 mL) the mixture was stirred for 3 h at 70 °C. Water was added and the precipitated polymer was filtrated off and washed subsequently with water (100 mL), acetone (50 mL), 2 *N* NaOH solution (50 mL) and again with water (100 mL). Finally the polymer was purified twice by redissolving it in 30 mL of DMF and subsequent precipitation with 2 *N* NaOH (100 mL), washed with plenty of water and dried *in vacuo* at 50 °C for 3 h.

5.3. Azo dyes:

5.3.1. Alkylsulphonazodyes:

2–[3–(2–Hydroxyethanesulphonyl) phenylazo] 4–methyl–phenol (**16**)



16

3.00 g (14.6 mmol) of 2–(3–amino–benzenesulphonyl)–ethanol was diazotised and the salt was coupled with 1.36 g (14.6 mmol) of *p*-cresol according to general procedure 5.2.1. The dye **16** was purified by FC (*t*–butylmethylether), followed by recrystallisation from ethanol: yellow–orange needles (3.00 g, 9.38 mmol, 75 %), m.p. 145 °C.

^{1}H NMR ($CDCl_3$): δ = 14.27 (s, 1 H, Ar–O<u>H</u>), 8.41 (t, $^4J_{13,\,11}$ = 1.8 Hz, 1 H, 13–H), 8.14 (ddd, $^3J_{11,\,10}$ = 7.9 Hz, $^4J_{11,\,13}$ = 1.8 Hz, $^4J_{11,\,9}$ = 1.1 Hz, 1 H, 11–H), 8.02 (ddd, $^3J_{9,\,10}$ = 7.9 Hz, $^4J_{9,\,13}$ = 1.8 Hz, $^4J_{9,\,11}$ = 1.1 Hz, 1 H, 9–H), 7.77 (d, $^4J_{3,\,5}$ = 4.4 Hz, 1 H, 3–H), 7.74 (t, $^3J_{10,\,11}$ = 7.9 Hz, 1 H, 10–H), 7.22 (dd, $^3J_{5,\,6}$ = 8.4 Hz, $^4J_{5,\,3}$ = 4.2 Hz, 1 H, 5–H), 6.95 (d, $^3J_{6,\,5}$ = 8.4 Hz, 1 H, 6–H), 4.77 (s, 1 H, Et–O<u>H</u>), 4.06 (t, $^3J_{15,\,14}$ = 5.3 Hz, 2 H, 15–H), 3.45 (t, $^3J_{14,\,15}$ = 5.3 Hz, 2 H, 14-H), 4.40 (s, 3 H, 7–H).

^{13}C NMR ($CDCl_3$): δ = 151.2 (s, C–8), 150.6 (s, C–1), 140.7 (s, C–12), 137.1 (s, C–2), 135.7 (d, C–5), 133.4 (d, C–10), 130.6 (d, C–11), 129.7 (s, C–4), 129.4 (d, C–9), 128.0 (d, C-3), 120.7 (d, C–13), 118.0 (d, C–6), 58.3 (t, C–14), 56.3 (t, C–15), 20.2 (q, C–7).

UV/vis ($CHCl_3$): λ_{max} (lg ε) = 242 nm (3.96), 254 (3.90), 330 (4.31), 412 (3.85).

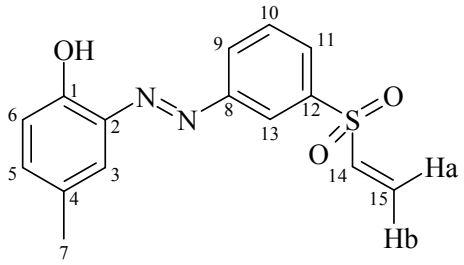
IR[1] (KBr): $\tilde{\nu}$ = 3479 cm^{-1} (m, val. aliph O–<u>H</u>), 3456 (m, val. arom. O–<u>H</u>), 3095 (w, val. arom. C–H), 3072 (w), 3060 (w), 3028 (w), 2987 (w), 2974 (w), 2956 (w, val. aliph. C–H, CH_3), 2931 (w), 2908 (w, val. aliph. C–H, CH_2), 2902 (w), 2883 (w), 2877 (w), 2870 (w),

2866 (w), 1625 (w, val. arom. C=C), 1596 (w), 1498 (s), 1445 (m, δ–CH_2), 1427 (w), 1407 (m, δ–CH_3), 1387 (w), 1358 (w), 131.9 (m), 1309 (s, val. asymm. S=O), 1300 (s), 1286 (m), 1273 (s), 1247 (m), 1219 (w), 1200 (m), 1148 (s), 1135 (vs, val. symm. S=O), 1075 (w), 1044 (s, val. C–O), 1015 (m), 996 (w), 905 (w), 798 (s, 1,3–disubstituted phenyl ring), 756 (m), 727 (m), 709 (m), 676 (1,3–disubstituted phenyl ring), 615 (s), 599 (m), 585 (m), 572 (m), 557 (m).

MS (EI): *m/z* (%): = 320 (80) [M^+], 135 (65) [M–$C_6H_4SO_2C_2H_4OH^+$], 107 (100) [*p*-$C_6H_4CH_3OH^+$].

EA: $C_{15}H_{16}N_2O_4S$ (320.37) calc. C 56.24 H 5.03 N 8.74 S 10.01;
found: C 56.27 H 4.98 N 8.51 S 10.06.

2–(3–Ethenesulphonyl–phenylazo) 4–methyl–phenol (**17**)



17

The dye **17** was obtained from 1.72 g (5.38 mmol) of compound **16** according to general procedure 5.2.2 without extraction with diethyl ether; 5 min after adding NaOH, the solution was neutralised with 2 *N* HCl and the precipitated dye was filtered off. The dye **17** was purified by FC (CH_2Cl_2), recrystallised from EtOH–water and appered as orange needles (1.30 g, 4.30 mmol, 80 %), m.p. 122 °C.

^{1}H NMR (DMSO–d_6): δ = 10.72 (s, 1 H, Ar–O<u>H</u>), 8.42 (t, $^4J_{13,\ 11}$ = 1.8 Hz, 1 H, 13–H), 8.34 (ddd, $^3J_{11,\ 10}$ = 7.9 Hz, $^4J_{11,\ 13}$ = 1.8 Hz, $^4J_{11,\ 9}$ = 1.1 Hz, 1 H, 11–H), 8.02 (ddd $^3J_{9,\ 10}$ = 7.9 Hz, $^4J_{9,\ 13}$ = 1.8 Hz, $^4J_{9,\ 11}$ = 1.1 Hz, 1 H, 9–H), 7.88 (t, $^3J_{10,\ 11}$ = 7.9 Hz, 1 H, 10-H), 7.57 (d, $^4J_{3,\ 5}$ = 1.3 Hz, 1 H, 3–H), 7.30 (dd, $^3J_{5,\ 6}$ = 8.4 Hz, $^4J_{5,\ 3}$ = 1.2 Hz, 1 H, 5–H), 7.25 (dd, $^3J_{14,\ Hb}$ = 9.8 Hz, $^3J_{14,\ Ha}$ = 16.4 Hz, 1 H, 14–H), 7.00 (d, $^3J_{6,\ 5}$ = 8.4 Hz, 1 H, 6–H), 6.45 (d, $^3J_{Ha,\ 14}$ = 16.4 Hz, 1 H, 15–Ha), 6.30 (d, $^3J_{Hb,\ 14}$ = 9.8 Hz, 1 H, 15–Hb), 4.30 (s, 3 H, 7–H).

^{13}C NMR (DMSO–d_6): δ = 153.5 (s, C–8), 154.0 (s, C–1), 141.0 (s, C–12), 138.3 (s, C–2), 138.2 (d, C–5), 135.5 (d, C–10), 131.0 (d, C–11), 130.1 (s, C–4), 129.1 (d, C–9), 128.7 (t, C-15), 128.6 (d, C–3), 120.8 (d, C–14), 120.1 (d, C–13), 118.3 (d, C–6), 19.9 (q, C–7).

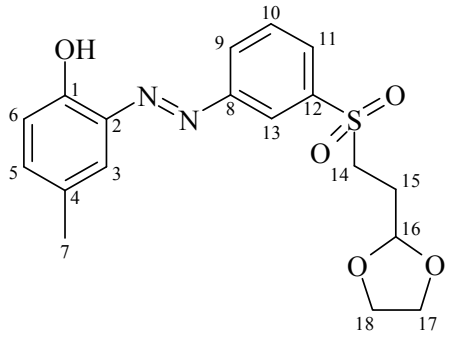
UV/vis ($CHCl_3$): λ_{max} (lg ε) = 242 nm (4.04), 328 (4.31), 438 (3.78).

IR[1] (KBr): $\tilde{\nu}$ = 3420 cm^{-1} (w, val. arom.O–H), 3074 (w, val. arom. C–H), 3055 (w, val. aliph. C=C), 3022 (w), 2947 (w, val. aliphat C–H, CH_3), 2943 (w), 2922 (w, val. aliphat C–H, CH_2), 2863 (w), 1625 (w, val. arom. C=C), 1591 (w), 1581 (w), 1494 (m), 1446 (m, δ–CH_2), 1429 (w, δ–CH_3), 1411 (w, aliph. C=C), 1386 (w), 1325 (m), 1313 (s, val. asymm. S=O), 1286 (m), 1269 (m), 1248 (m), 1199 (m), 1172 (w), 1138 (vs, val. symm. S=O), 1091 (w, val. C–O), 1072 (w), 996 (w), 982 (m), 948 (w), 908 (w, δ aliph. C=C), 819 (m), 802 (s), 782 (m, 1,3-disubs. phenyl ring), 741 (s), 705 (m, 1,3–disubs. phenyl ring), 685 (w), 672 (w), 644 (m), 603 (w), 575 (w), 567 (w), 527 (w), 504 (w), 477 (w), 436 (w).

MS (EI): *m/z* (%): = 302 (28) [M^+], 135 (36) [M–$C_6H_4SO_2C_2H_3^+$], 107 (100) [*p*–$C_6H_4CH_3OH^+$].

EA: $C_{15}H_{14}N_2O_3S$ (302.35) calc. C 59.59 H 4.67 N 9.26
found: C 59.96 H 4.65 N 8.95.

2–{3–[2–([1,3] Dioxolan–2–yl) ethanesulphonyl] phenylazo} 4–methyl–phenol (**18**)



18

1.55 g (5.13 mmol) of reagent **17** was irradiated for 1 h as is described in general procedure 5.2.3 (route A). Purification was achieved by FC from $CHCl_3$/*c*–C_6H_{12}/EtOAc (5/3/2). The product **18** was recrystallised from EtOH and obtained orange needles after redissolving in $CHCl_3$ and evaporation to dryness (0.48 g, 1.28 mmol, 25 %).

Route B: 4.90 g (11.3 mmol) of aniline **23a** was diazotised and coupled with 1.22 g (11.3 mmol) *p*-cresol as described in general procedure 5.2.1. The dye **18** was purified by FC (*t*-butylmethylether), followed by recrystallisation from EtOH: dark orange needles (3.40 g, 9.04 mmol, 80 %), m.p. 160 °C.

^{1}H NMR ($CDCl_3$): δ = 12.30 (s, 1 H, Ar–O<u>H</u>), 8.40 (t, $^4J_{13,11}$ = 1.8 Hz, 1 H, 13–H), 8.13 (ddd, $^3J_{11,10}$ = 7.9 Hz, $^4J_{11,13}$ = 1.8 Hz, $^4J_{11,9}$ = 1.1 Hz, 1 H, 11–H), 7.99 (ddd, $^3J_{9,10}$ = 7.9 Hz, $^4J_{9,13}$ = 1.8 Hz, $^4J_{9,11}$ = 1.1 Hz, 1 H, 9–H), 7.78 (d, $^4J_{3,5}$ = 1.5 Hz, 1 H, 3–H), 7.73 (t, $^3J_{10,11}$ = 7.9 Hz, 1 H, 10–H), 7.21 (dd, $^3J_{5,6}$ = 8.4 Hz, $^4J_{5,3}$ = 1.5 Hz, 1 H, 5–H), 6.96 (d, $^3J_{6,5}$ = 8.4 Hz, 1 H, 6–H), 4.98 (t, $^3J_{16,15}$ = 3.9 Hz, 1 H, 16–H), 3.90 (m, AA'BB', 4 H, 17–, 18–H), 3.31 (m, 2 H, 14-H), 2.17 (s, 3 H, 7–H), 2.15 (m, 2 H, 15–H).

^{13}C NMR ($CDCl_3$): δ = 151.1 (s, C–8), 150.6 (s, C–1), 140.6 (s, C–12), 137.1 (s, C–2), 135.6 (d, C–5), 133.4 (d, C–10), 130.4 (d, C–11), 129.7 (s, C–4), 129.6 (d, C–9), 127.7 (d, C–3), 121.0 (d, C–13), 118.0 (d, C–6), 101.6 (d, C–16), 65.1 (t, C–17, –18), 50.6 (t, C–14), 26.9 (t, C–15), 20.2 (q, C–7).

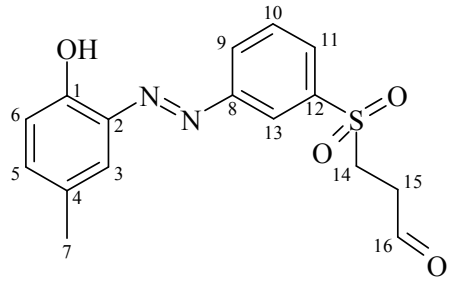
UV/vis ($CHCl_3$): λ_{max} (lg ε) = 240 nm (3.91), 254 (3.91), 328 (4.31), 412 (3.85).

IR[1] (KBr): $\tilde{\nu}$ = 3444 cm^{-1} (w, val. arom O–<u>H</u>), 3094 (w, val. arom C–H), 3067 (w), 3024 (w), 2963 (w, val. aliph. C–H, CH_3), 2946 (w), 2914 (w, val. aliph. C–H, CH_2), 2904 (w), 2859 (w), 2791 (w), 2786 (w), 2779 (w), 2758 (w), 2721 (w), 1624 (w, val. arom C=C), 1595 (w), 1497 (s), 1445 (m, δ–CH_2), 1404 (m, δ–CH_3), 1397 (m), 1322 (m), 1309 (s, val. asymm. S=O), 1303 (s), 1285 (m), 1271 (s, acetal C–O–C), 1242 (m), 1232 (w), 1199 (m), 1134 (vs, val. symm. S=O), 1072 (m, val. C–O), 1052 (m), 1031 (s), 1014 (m), 949 (w), 944 (w), 902 (w), 890 (m), 808 (m), 797 (s), 785 (s, 1,3–disubs. phenyl ring), 777 (m), 716 (m), 711 (w), 676 (s, 1,3-disubs. phenyl ring), 567 (m), 544 (w), 503 (s).

MS (EI): *m/z* (%): = 376 (90) [M^+], 135 (86) [M–$C_6H_4SO_2C_2H_4CH(OCH_2)_2^+$], 107 (100) [*p*-$C_6H_4CH_3OH^+$].

EA: $C_{18}H_{20}N_2O_5S$ (376.43) calc. C 57.43 H 5.36 N 7.44 S 8.52
found: C 57.48 H 5.55 N 7.43 S 8.47.

3–[3–(2–Hydroxi–5–methyl–phenylazo) benzenesulphonyl] propanal (**19**)



19

Cleavage of 1.23 g (3.27 mmol) of acetal **18** according to general procedure 5.2.4, and purification by FC with $CHCl_3$/*c*–C_6H_{12}/EtOAc (5/3/2), followed by recrystallisation from EtOH gave the product **19** as orange needles (0.65 g, 1.96 mmol, 60 %), m.p. 130 °C.

^{1}H NMR ($CDCl_3$): δ = 14.18 (s, 1 H, Ar–OH), 9.70 (s, 1 H, 16–H), 8.31 (t, $^4J_{13,\,11}$ = 1.8 Hz, 1 H, 13–H), 8.08 (ddd, $^3J_{11,\,10}$ = 7.9 Hz, $^4J_{11,\,13}$ = 1.8 Hz, $^4J_{11,\,9}$ = 1.0 Hz, 1 H, 11–H), 7.93 (ddd, $^3J_{9,\,10}$ = 7.9 Hz, $^4J_{9,\,13}$ = 1.8 Hz, $^4J_{9,\,11}$ = 1.0 Hz, 1 H, 9–H), 7.70 (d, $^4J_{3,\,5}$ = 1.6 Hz, 1 H, 3–H), 7.65 (t, $^3J_{10,\,11}$ = 7.9 Hz, 1 H, 10–H), 7.15 (dd, $^3J_{5,\,6}$ = 8.4 Hz, $^4J_{5,\,3}$ = 1.6 Hz, 1 H, 5–H), 6.89 (d, $^3J_{6,\,5}$ = 8.4 Hz, 1 H, 6–H), 3.42 (t, $^3J_{14,\,15}$ = 7.5 Hz, 2 H, 14–H), 4.97 (t, $^3J_{15,\,14}$ = 7.5 Hz, 2 H, 15–H), 4.32 (s, 3 H, 7–H).

^{13}C NMR ($CDCl_3$): δ = 196.5 (d, C–16), 151.3 (s, C–8), 150.6 (s, C–1), 140.4 (s, C–12), 137.2 (s, C–2), 135.8 (d, C–5), 133.3 (d, C–10), 130.6 (d, C–11), 129.7 (s, C–4), 129.4 (d, C-9), 128.0 (d, C-3), 120.8 (d, C–13), 118.0 (d, C–6), 49.0 (t, C–14), 36.4 (t, C–15), 20.2 (q, C–7).

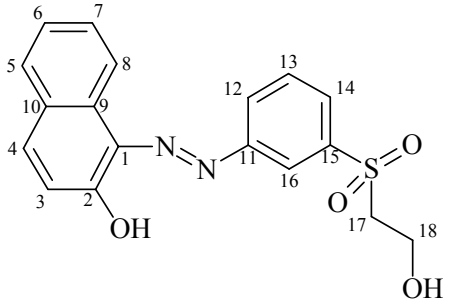
UV/vis ($CHCl_3$): λ_{max} (lg ε) = 242 nm (3.96), 254 (3.92), 330 (4.28), 412 (3.83).

IR[1] (KBr): $\tilde{\nu}$ = 3440 cm^{-1} (w, val. arom. O–H), 3094 (w, val. arom. C–H), 3065 (w), 3028 (w), 2992 (w, val. aliph. C–H, CH_3), 2922 (w, val. aliph. C–H, CH_2), 2842 (m, val. asymm. C-HO), 2736 (w, val. symm. C–HO, Fermi`s doublet), 1730 (s, val. C=O), 1714 (w), 1624 (w, arom C=C), 1596 (w), 1498 (m), 1445 (w, δ–CH_2), 1426 (w, δ–CH_3), 1407 (w), 1387 (w), 1357 (w), 1343 (w), 1309 (s, val. asymm. S=O), 1303 (m), 1285 (w), 1272 (m), 1246 (w), 1234 (w), 1218 (w), 1199 (w), 1147 (s), 1136 (vs, val. symm. S=O), 1087 (w, val. C–O), 1074 (w), 902 (w), 798 (m), 784 (m, 1,3–disubs. phenyl ring.), 715 (w), 680 (w), 596 (w), 583 (w), 570 (m).

MS (EI): *m/z* (%): = 332 (65) [M^+], 135 (77) [M–$C_6H_4SO_2C_2H_4CHO^+$], 107 (100) [*p*-$C_6H_4CH_3OH^+$].

EA: $C_{16}H_{16}N_2O_4S$ (332.38): calc. C 57.82 H 4.85 N 8.43 S 9.65
found: C 57.80 H 4.98 N 8.07 S 9.48

2–[3–(2–Hydroxi–ethanesulphonyl) phenylazo] naphthalen–2–ol (**20**)



20

1.19 g (5.00 mmol) of 2–(3–amino–benzenesulphonyl)–ethanol was diazotised and the salt was coupled with 0.72 g (5.00 mmol) of 2–naphthol according to general procedure 5.2.1. The dye **20** was purified by FC with EtOAc/C_6H_{12} (1/3), followed by recrystallisation from EtOH: orange needles (1.64 g, 4.60 mmol, 94 %), m.p. 171 °C.

^{1}H NMR ($CDCl_3$): δ (ppm) = 16.02 (br. s, 1 H, ArOH), 8.44 (d, $^3J_{5,6}$ = 8.5 Hz, 1 H, 5–H), 8.22 (s, 1 H, 16–H), 7.87 (d, $^3J_{14,13}$ = 7.9 Hz, 1 H, 14–H), 7.77 (d, $^3J_{12,13}$ = 7.9 Hz, 1 H, 12-H), 7.69 (d, $^3J_{4,3}$ = 9.4 Hz, 1 H, 4–H), 7.65 (t, $^3J_{13,14}$ = 7.9 Hz, 1 H, 13–H), 7.54 (m, 2 H, 8–, 6–H), 7.40 (td, $^4J_{7,5}$ = 1.1 Hz, $^3J_{7,6}$ = 8.5 Hz, 1 H, 7–H), 6.76 (d, $^3J_{3,4}$ = 9.4 Hz, 1 H, 3-H), 4.08 (t, $^3J_{17,18}$ = 5.3 Hz, 2 H, 17–H), 3.46 (t, $^3J_{18,17}$ = 5.5 Hz, 2 H, 18–H), 4.01 (br.s, 1 H, EtOH).

^{13}C NMR ($CDCl_3$): δ = 156.0 (s, C–2), 145.3 (s, C–11), 141.9 (d, C–4), 140.4 (s, C–15), 133.1 (s, C–9), 130.7 (d, C–13), 129.4 (d, C–8), 128.8 (d, C–6), 128.3 (s, C–10), 126.7 (d, C-7), 126.5 (s, C–1), 125.1 (d, C–12, –3), 123.0 (d, C–14), 124.1 (d, C–5), 116.7 (d, C–16), 58.3 (t, C–18), 56.3 (t, C-17).

UV/vis (DMSO): λ_{max} (lg ε) = 254 nm (4.04), 260 (4.10), 300 (4.00), 478 (4.21).

UV/vis (1,4–dioxane): λ_{max} (lg ε) = 230 nm (4.37), 254 (3.89 sh), 302 (3.78), 424 (3.90 sh), 472 (4.04), 500 (3.93 sh).

UV/vis (EtOH): λ_{max} (lg ε) = 210 nm (4.56), 228 (4.58), 254 (4.06 sh), 302 (3.97), 424 (4.10 sh), 472 (4.23).

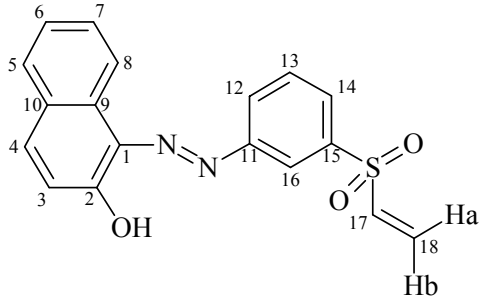
UV/vis ($CHCl_3$): λ_{max} (lg ε) = 242 nm (4.28), 264 (4.04 sh), 304 (4.00), 420 (4.06 sh), 476 (4.26).

IR[2] (KBr): $\tilde{\nu}$ = 3470 cm^{-1} (m, val. ArO–H, dimer structures), 3415 (m, val. ArO–H), 3080 (w, val. arom. C–H), 3025 (w, val. arom. C–H), 2974 (w, val. aliph. C–H, CH_3), 2918 (w, val. aliph. C–H, CH_2), 2879 (w), 1615 (m, val. arom. C=C), 1596 (w), 1554 (m), 1501 (vs), 1441 (s, δ–CH_2), 1393 (m), 1304 (s, val. asymm. S=O), 1287 (m), 1253 (m), 1228 (w), 1207 (s), 1156 (s, val. C–O), 1124 (vs, val. symm. S=O), 1070 (m), 1017 (m), 984 (m), 863 (w), 832 (m), 790 (m, 1,3–disubs. phenyl ring), 751 (m), 716 (s, 1,3–disubs. phenyl ring), 683 (m), 672 (m), 647 (m), 597 (m).

MS (EI): *m/z* (%): = 356 (57) [M^+], 338 (9) [M–H_2O^+], 247 (11) [M–$SO_2C_2H_4OH^+$], 171 (37) [M–$C_6H_4SO_2C_2H_4OH^+$], 159 (21) [$C_{10}H_6OH\,NH_2^+$], 143 (100) [$C_{10}H_7O^+$].

EA: $C_{18}H_{16}N_2O_4S$ (356.41): calc. C 60.66 H 4.53 N 7.86
found: C 60.45 H 4.34 N 7.55

2–(3–Ethenesulphonyl–phenylazo) naphthalen–2–ol (**21**)



21

The dye **21** has been reported in reference,[62c] but no synthetic method is given for its preparation. It was obtained from 1.56 g (4.38 mmol) of compound **20** according to general procedure 5.2.2 without diethyl ether extraction. After pouring a 2 *N* NaOH solution to the

reaction mixture, it was neutralised with 2*N* HCl, and the precipitated dye was filtered off. After purification by FC (CH_2Cl_2) and recrystallisation from EtOH dye **21** was obtained as orange needles (1.40 g, 4.14 mmol, 95 %), m.p. 174 °C. (lit.[62c] 132–134 °C). Because of the great difference in the melting point, dye **21** was completely characterised.

^{1}H NMR (DMSO–d_6): δ = 15.6 (s, 1 H, ArO<u>H</u>), 8.45 (d, $^3J_{5,6}$ = 8.2 Hz, 1 H, 5–H), 8.26 (t, $^4J_{16,14}$ = 1.2 Hz, 1 H, 16-H), 8.16 (m, 1 H, 14–H), 7.95 (d, $^3J_{4,3}$ = 9.5 Hz, 1 H, 4–H), 7.78 (m, 2 H, 12–, 13–H), 7.76 (d, $^3J_{8,7}$ = 7.5 Hz, 1 H, 8–H), 7.63 (td, $^4J_{6,8}$ = 1.2 Hz, $^3J_{6,5}$ = 7.3 Hz, 1 H, 6–H), 7.47 (td, $^4J_{7,5}$ = 1.2 Hz, $^3J_{7,8}$ = 8.1 Hz, 1 H, 7–H), 7.32 (dd, $^3J_{17,18\text{–Hb}}$ = 9.8 Hz, $^3J_{17,18\text{–Ha}}$ = 16.4 Hz, 1 H, 17–H), 6.85 (d, $^3J_{3,4}$ = 9.5 Hz, 1 H, 3–H), 6.46 (d, $^3J_{18\text{-Ha},17}$ = 16.4 Hz, 1H, 18–Ha), 6.31 (d, $^3J_{18\text{–Hb},17}$ = 9.8 Hz, 1 H, 18–Hb).

^{13}C NMR (DMSO–d_6): δ = 174.3 (s, C–2), 145.3 (s, C–11), 141.4 (s, C–15), 141.2 (d, C–4), 138.2 (d, C–17), 134.5 (s, C–9), 131.1 (d, C–13), 129.8 (s, C–1), 129.5 (d, C–6), 129.4 (t, C-18), 129.1 (d, C–8), 128.0 (s, C–10), 126.5 (d, C–7), 125.2 (d, C–12), 124.6 (d, C–3), 123.1 (d, C–14), 121.5 (d, C–5), 116.7 (d, C–16).

UV/vis (DMSO): λ_{max} (lg ε) = 260 nm (4.10), 300 (4.02), 336 (3.70 sh), 480 (4.21), 554 (3.60 sh).

UV/vis (1,3–dioxolane): λ_{max} (lg ε) = 236 nm (4.46), 260 (4.09 sh), 304 (3.98), 488 (4.21).

UV/vis (EtOH): λ_{max} (lg ε) = 226 nm (4.64), 254 (4.05 sh), 302 (3.92), 472 (4.22).

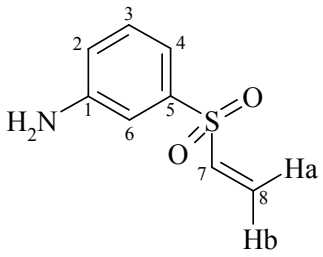
UV/vis ($CHCl_3$): λ_{max} (lg ε) = 242 nm (4.32), 262 (4.08 sh), 304 (4.01), 418 (4.05 sh), 476 (4.26).

IR[2] (KBr): $\tilde{\nu}$ = 3113 cm^{-1} (w, val. ArO–H), 3064 (w, val. arom. C–H), 3021 (w), 2899 (w, val. aliph. C-H, CH_2), 2371 (w), 1978 (w, val. aliph. C=C), 1708 (m), 1612 (m, val. arom. C=C), 1594 (m), 1564 (m), 1496 (vs), 1442 (s, δ–CH_2), 1395 (m), 1380 (m), 1253 (s), 1221 (m), 1201 (w), 1175 (s), 1155 (m), 1130 (s, val. asymm. S=O), 1096 (m), 1068 (m, val. C–O), 986 (s), 953 (m), 910 (m), 884 (m), 853 (m), 797 (m, 1,3–disubs. phenyl ring), 760 (s), 735 (m), 690 (m), 654 (m), 593 (m).

MS (EI): *m/z* (%): = 338 (70) [M^+], 321 (4) [$M–OH^+$], 183 (14) [$M–C_{10}H_9NO^+$], 171 (36) [$M\text{-}C_6H_4SO_2C_2H_4OH^+$], 159 (15) [$C_{10}H_6OH\,NH_2^+$], 143 (100) [$C_{10}H_7O^+$].

EA: $C_{18}H_{14}N_2O_3S$ (338.39): calc. C 63.89 H 4.17 N 8.28
found: C 63.66 H 4.11 N 7.96

3–Ethenesulphonylaniline (**22**)



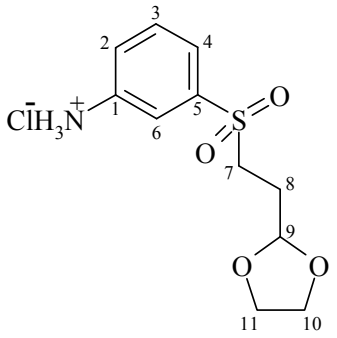
22

The aniline **22** was prepared from 3.00 g (14.6 mmol) of 2–(3–amino–benzenesulphonyl)–ethanol according to general procedure 5.2.2 and purified by FC (diethyl ether). All spectroscopic data of the crude product (4.00 g, 10.9 mmol, 86 %) correspond to those found in the literature.[142]

^{1}H NMR: ($CDCl_3$, 200.13 MHz): δ = 7.32 (d, $^3J_{4,3}$ = 7.7 Hz, 1 H, 4–H), 7.24 (t, $^4J_{6,2}$ = 1.5 Hz, 1 H, 6–H), 7.16 (m, 1 H, 3–H), 6.87 (ddd, $^3J_{2,3}$ = 7.7 Hz, $^4J_{2,6}$ = 1.5 Hz, $^4J_{2,4}$ = 1.5 Hz, 1 H, 2–H), 6.65 (dd, $^3J_{7,8Hb}$ = 9.6 Hz, $^3J_{7,8Ha}$ = 16.5 Hz, 1 H, 7–H), 6.41 (d, $^3J_{8Ha,7}$ = 16.5 Hz, 1 H, 8–H, Ha), 6.02 (d, $^3J_{8Hb,7}$ = 9.6 Hz, 1 H, 8–H, Hb), 4.03 (br. s, 2 H, N<u>H</u>).

^{13}C NMR (acetone–d_6, 50.32 MHz): δ = 147.5 (s, C–1), 140.2 (s, C–5), 138.5 (d, C–3), 130.2 (d, C–4), 127.3 (t, C–8), 119.7 (d, C–6), 117.2 (d, C–7), 113.2 (d, C–6).

3–[2–([1,3] Dixolan–2–yl) ethanesulphonyl] aniline (**23**), as hydrochloride (**23a**)



23a

The aniline **23** was prepared according to general procedure 5.2.3 from 0.33 g (1.80 mmol) of reagent **7** and purified by FC (diethylether) and was converted into its hydrochloride (**23a**). The product **8** appeared as an oil, which decomposed during attempted distillation (150 °C/ 0.5 mm Hg). Compound **23a** gave white crystals (0.50 g, 1.70 mmol, 94 %) after recrystallisation from MeOH, m.p. 135 °C.

^{1}H NMR (**23a**/ DMSO–d_6): δ = 7.58 (m, 3 H, 2–, 4–, 6–H), 7.44 (d, $^3J_{3,4}$ = 7.5 Hz, 1 H, 3-H), 7.20 (br. s., 3 H, $N\underline{H}_3^+$), 4.90 (t, $^3J_{9,8}$ = 4.2 Hz, 1 H, 9–H), 3.85 (m, 4 H, 10–H, 11–H), 3.30 (m, 2 H, 7–H), 1.85 (m, 2 H, 8–H).

^{13}C NMR (**23a**/ DMSO–d_6): δ = 139.9 (s, C–5), 139.5 (s, C–1), 130.7 (d, C–3), 124.8 (d, C–4), 121.7 (d, C–2), 118.2 (d, C–6), 101.0 (d, C–9), 64.5 (t, C–10, –11), 50.0 (t, C–7), 27.0 (t, C–8).

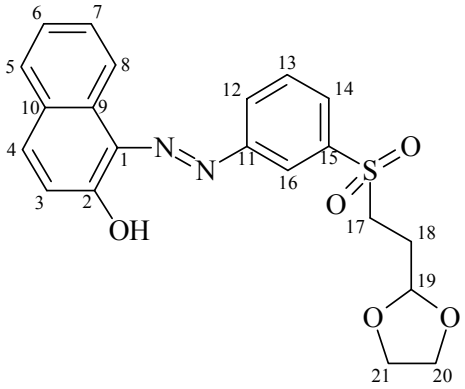
UV/vis (DMSO): λ_{max} (lg ε) = 262 nm (4.33), 276 (4.16).

IR[1] (KBr): $\tilde{\nu}$ = 3442 cm^{-1} (br. m., val. $ArNH_2$), 3067 (w, val. arom. C–H), 2931 (m, val. aliph. C–H, CH_3), 2883 (s, val. aliph. C–H, CH_2), 2871 (s), 2634 (w), 2580 (w), 1605 (w, val. arom. C=C), 1575 (w, δ–$ArNH_2$), 1543 (m), 1479 (m, δ–CH_2), 1441 (w), 1412 (w, δ–CH_3), 1386 (w), 1320 (m), 1299 (m), 1284 (w, acetal C–O–C), 1239 (w), 1215 (w), 1138 (vs, val. symm. S=O), 1093 (w, val. C–O), 1081 (w), 1055 (w), 1031 (w), 1026 (w), 945 (w), 896 (w), 883 (w), 788 (m, 1,3–disubs. phenyl ring), 780 (w), 712 (w), 702 (m, 1,3–disubs. phenyl ring), 676 (w), 573 (w), 545 (w), 530 (w), 525 (w), 488 (m).

MS (EI): *m/z* (%): = 257 (8) [M^+], 164 (69) [M–$C_6H_4NH_2^+$], 73 (100) [$CH(OCH_2)_2^+$].

High–resolution MS: $C_{11}H_{15}NO_4S$ calc. 257.07218
found: 257.07265.

1–{3–[2–([1,3] Dioxolan–2–yl) ethanesulphonyl] phenylazo} naphthalen–2–ol (**39**)



39

0.90 g (3.06 mmol) of aniline **23a** was diazotised and was coupled with 2–naphthol according to general procedure 5.2.1. Purification by FC $CHCl_3$/*c*–C_6H_{12}/EtOAc (5/3/2), followed by recrystallisation from acetone–water, afforded orange needles from dye **39** (1.00 g, 4.43 mmol, 80 %), m.p. 190 °C.

^{1}H NMR (DMSO–d_6): δ = 15.49 (br. s, 1 H, Ar–O<u>H</u>), 8.50 (d, $^3J_{5,6}$ = 7.9 Hz, 1 H, 3–H), 8.30 (d, $^4J_{16,14}$ = 1.7 Hz, 1 H, 16–H), 8.20 (dt, $^3J_{14,13}$ = 7.7 Hz, $^4J_{14.16}$ = 1.7 Hz, 1 H, 14–H), 7.95 (d, $^3J_{4,3}$ = 9.5 Hz, 1 H, 4–H), 7.82 (m, 1 H, 12–H), 7.80 (t, $^3J_{13.14}$ = 7.8 Hz, 1 H, 13–H), 7.76 (d, $^3J_{8,7}$ = 7.7 Hz, 1 H, 7–H), 7.61 (td, $^3J_{6,7}$ = 7.9 Hz, $^3J_{6,8}$ = 1.0 Hz, 1 H, 6–H), 7.49 (td, $^3J_{7,6}$ = 7.9 Hz, $^3J_{7,5}$ = 1.0 Hz, 1 H, 7–H), 6.86 (d, $^3J_{3,4}$ = 9.5 Hz, 1 H, 3–H), 4.94 (t, $^3J_{19,18}$ = 4.3 Hz, 1 H, 19-H), 3.86 (m, AA'BB', 4 H, 20–, 21–H), 3.44 (m, 2 H, 17–H), 1.95 (m, 2 H, 18–H).

^{13}C NMR (DMSO–d_6): δ = 174.2 (s, C–2), 145.4 (s, C–15), 141.3 (d, C–4), 140.2 (s, C–11), 134.5 (s, C–9), 134.6 (s, C–1), 131.0 (d, C–12), 130.0 (s, C–10), 129.4 (d, C–6), 129.0 (d, C-8), 128.0 (d, C–7), 126.4 (d, C–13), 124.7 (d, C–3), 123.1 (d, C–14), 121.6 (d, C–6), 117.4 (d, C–16), 101.1 (d, C–19), 64.5 (t, C–20, –21), 49.8 (t, C–17), 26.9 (t, C–18).

UV/vis (DMSO): λ_{max} (lg ε) = 262 nm (4.40), 418 (4.09), 476 (4.23).

UV/vis (1,4–dioxane): λ_{max} (lg ε) = 232 nm (4.60), 268 (4.10 sh), 302 (3.92), 472 (4.22), 500 (4.23).

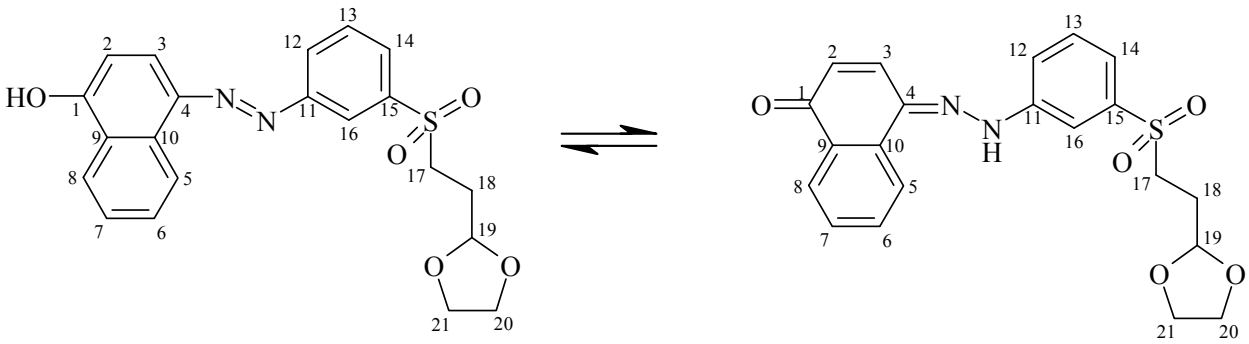
UV/vis (EtOH): λ_{max} (lg ε) = 210 nm (4.52), 228 (4.57), 266 (4.01 sh), 302 (3.91), 472 (4.23), 500 (4.19 sh).
UV/vis ($CHCl_3$): λ_{max} (lg ε) = 242 nm (4.30), 262 (4.05 sh), 304 (3.91), 424 (4.08 sh), 476 (4.26).

IR[1] (KBr): $\tilde{\nu}$ = 3445 cm^{-1} (s, assoc. ArO–H), 3066 (w, val. arom. C–H), 2968 (m, val. aliph. C–H, CH_3), 2943 (w, val. aliph C–H, CH_2), 2928 (w), 2885 (m), 1620 (m, arom. val C=C), 1599 (m), 1584 (m), 1567 (s), 1556 (m), 1506 (m), 1475 (m, δ–CH_2), 1453 (m), 1442 (m), 1405 (s, δ–CH_3), 1386 (m), 1331 (m), 1304 (vs, val asymm. S=O), 1276 (m), 1256 (s, acetal C-O-C), 1228 (s), 1208 (vs), 1178 (s), 1156 (s), 1139 (vs, val symm. S=O), 1079 (m, val C–O), 1047 (m), 1029 (m), 993 (m), 985 (m), 948 (m), 862 (s), 835 (s), 804 (m, 1,3–disubs. phenyl ring), 788 (m), 757 (s), 703 (m, 1,3–disubs. phenyl ring), 682 (m), 605 (m), 545 (m), 542 (m), 495 (s).

MS (EI): *m/z* (%): = 412 (85) [M^+], 384 (6) [M–CO^+], 311 (19) [M–$C_2H_4C(OCH_2)_2^+$], 171 (48) [$C_{10}H_6OHNN^+$], 143 (100) [$C_{10}H_6OH^+$].

EA: $C_{21}H_{20}N_2O_5S$ (412.46):	calc.	C 61.15 H 4.89 N 6.79
	found	C 61.01 H 4.89 N 6.57.

4–{3–[2–([1,3] Dioxolan–2–yl) ethanesulphonyl] phenylazo} naphthalen–1–ol (**40**)



40

According to general procedure 5.2.1 0.56 g (1.91 mmol) aniline **23a** was diazotised and was coupled with 0.280 g (1.90 mmol) of 1–naphthol. Purification by FC with $CHCl_3$/c–C_6H_{12}/EtOAc (5/3/2) and recrystallisation from acetone–water gave the dye **40** as orange needles (0.55 g, 1.34 mmol, 70. %), m.p. 195 °C.

^{1}H NMR (DMSO–d_6, 100 °C): δ = 11.60 (br. s, 1H, Ar–O<u>H</u>), 8.75 (d, $^{3}J_{8,7}$ = 8.0 Hz, 1 H, 8-H), 8.20 (br. d., 1 H, $^{3}J_{5,6}$ = 8.0 Hz, 5–H), 8.19 (s, 1 H, 16–H), 8.11 (br. d, $^{3}J_{14,13}$ = 7.9 Hz, 1 H, 14–H), 8.05 (d, $^{3}J_{3,2}$ = 9.1 Hz, 1 H, 3–H), 7.83 (br. d, 1 H, 12–H), 7.79 (br. t, $^{3}J_{13,14}$ = 7.6 Hz, 1 H, 13–H), 7.73 (td, $^{4}J_{7,5}$ = 1.3 Hz, $^{3}J_{7,6}$ = 7.0 Hz, 1 H, 7–H), 7.58 (td, $^{4}J_{6,8}$ = 1.3 Hz, $^{3}J_{6,7}$ = 7.0 Hz, 1 H, 6–H), 6.96 (d, $^{3}J_{2,3}$ = 9.1 Hz, 1 H, 2–H), 4.96 (t, $^{3}J_{19,18}$ = 4.3 Hz, 1 H, 19–H), 3.80 (m AA'BB', 4 H, 20–, 21–H), 3.43 (t, $^{3}J_{17,18}$ = 7.8 Hz, 2 H, 17–H), 1.92 (m, 2 H, 18–H).

^{13}C NMR (DMSO–d_6, 104.2 °C): δ = 139.9 (s, C–11), 130.9 (d, C–12, –13), 129.0 (d, C–7), 126.4 (d, C–6), 123.0 (d, C–5), 124.6 (d, C–8), 120.6 (s, C–4), 101.1 (d, C–19), 64.5 (t, C–20, –21), 50.0 (t, C–17), 27.0 (t, C–18).

UV/vis (DMSO): λ_{max} (lg ε) = 254 nm (4.12), 280 (4.15), 450 (4.22), 558 (3.81).

UV/vis (1,4–dioxane):λ_{max} (lg ε) = 222 nm (4.34), 234 (4.33), 272 (4.11), 310 (3.69 sh), 426 (4.16).

UV/vis (EtOH): λ_{max} (lg ε) = 206 nm (4.58), 236 (4.23), 306 (3.78 sh), 442 (4.28), 540 (3.57 sh).

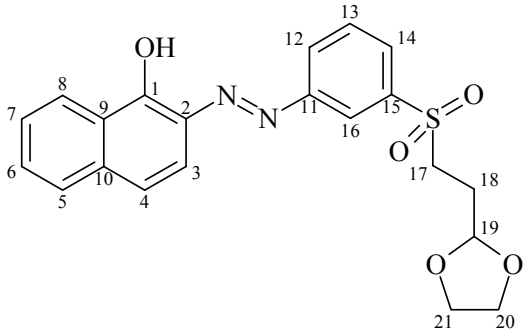
UV/vis ($CHCl_3$): λ_{max} (lg ε) = 242 nm (14.20), 278 (4.20), 312 (3.85 sh), 446 (4.39).

IR[2] (KBr): $\tilde{\nu}$ = 3237 cm^{-1} (m, val. ArO–H), 3122 (w), 3066 (w, val. arom. C–H), 2965 (w, val. aliph. C-H, CH_3), 2920 (w, val. aliph. C–H, CH_2), 1618 (m, val. arom. C=C), 1591 (vs), 1535 (vs), 1446 (s, δ–CH_2), 1408 (s, δ–CH_3), 1351 (m), 1304 (s, val. asymm. S=O), 1250 (s, acetal C-O–C), 1135 (s, val. symm. S=O), 1072 (m, val. C–O), 1009 (s), 870 (m), 789 (m, 1,3-disubs. phenyl ring), 763 (s), 705 (m, 1,3–disubs. phenyl ring), 682 (m).

MS (EI): *m/z* (%): = 412 (45) [M^+], 384 (9) [M–CO^+], 338 (10) [M–$CH_2(OCH_2)_2^+$], 143 (100) [$C_{10}H_6OH^+$].

EA: $C_{21}H_{20}N_2O_5S$ (412.46): calc. C 61.15 H 4.89 N 6.79 S 7.77
found C 61.30 H 5.05 N 6.93 S 7.74.

2–{3–[2–([1,3] Dioxolan–2–yl) ethanesulphonyl] phenylazo} naphthalen–1–ol (**41**)



41

The dye **41** was formed as a by–product in the preparation of compound **40**. Purification as described above afforded orange needles (0.15 g, 0.46 mmol, 10 %), m.p. 211 °C.

^{1}H NMR (DMSO–d_6): δ = 14.40 (br. s, 1 H, Ar–O<u>H</u>), 8.36 (s, 1 H, 16–H), 8.35 (d, $^{3}J_{5,6}$ = 7.8 Hz, 1 H, 5–H), 8.18 ("d", $^{3}J_{14,13}$ = 7.7 Hz, 1 H, 14–H), 7.83 (m, 3 H, 8–, 12–, 13-H), 7.80 (td, $^{3}J_{6,7}$ = 7.8 Hz, $^{4}J_{6,8}$ = 1.1 Hz, 1 H, 6–H), 7.58 (td, $^{3}J_{7,6}$ = 7.8 Hz, $^{4}J_{5,6}$ = 1.1 Hz, 1 H, 7–H), 7.43 (d, $^{3}J_{3,4}$ = 9.3 Hz, 1 H, 3–H), 7.24 (d, $^{3}J_{4,3}$ = 9.3 Hz, 1 H, 4-H), 4.93 (t, $^{3}J_{19,18}$ = 4.2 Hz, 1 H, 19-H), 3.80 (m, AA'BB', 4 H, 20–, 21–H), 3.44 (m, 2 H, 17–H), 1.92 (m, 2 H, 18–H).

^{13}C NMR (DMSO–d_6): δ = 165.7 (s, C–1), 140.1 (s, C–15, –11), 136.7 (s, C–10), 133.3 (s, C–2), 134.1 (d, C–12), 130.8 (d, C–3), 128.0 (d, C–7), 126.8 (d, C–13), 125.9 (d, C–4), 125.7 (d, C–14), 124.6 (d, C–5), 123.1 (d, C–8), 121.6 (d, C–6), 117.3 (d, C–16), 103 (s, C-9), 101.1 (d, C–19), 64.5 (t, C–20, –21), 49.8 (t, C–17), 26.9 (t, C–18).

UV/vis (DMSO): λ_{max} (lg ε) = 258 nm (4.05), 294 (4.21), 348 (4.06), 500 (4.16), 528 (4.10 sh), 572 (3.77 sh).

UV/vis (1,4–dioxane): λ_{max} (lg ε) = 226 nm (4.37), 290 (4.29), 298 (4.27), 360(4.11), 492 (4.29).

UV/vis (EtOH): λ_{max} (lg ε) = 204 nm (4.26), 240 (4.01 sh), 288 (4.15), 296 (4.12 sh), 358 (3.92), 488 (4.10).

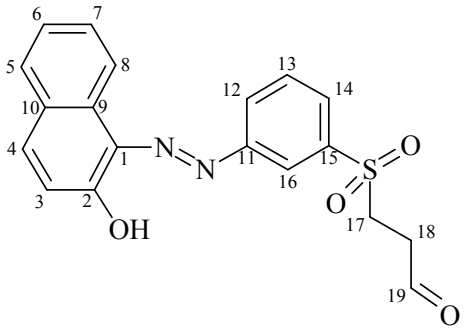
UV/vis ($CHCl_3$): λ_{max} (lg ε) = 242 nm (4.20), 292 (4.31), 298 (4.29 sh), 362 (4.13), 494 (4.29).

IR[1] (KBr): $\tilde{\nu}$ = 3442 cm^{-1} (m, assoc. ArO–H), 3099 (w), 3072 (w, val. arom. C–H), 3048 (w), 2983 (m), 2961 (m, val. aliph. C–H, CH_3), 2925 (m, val. aliph C–H, CH_2), 2906 (m), 2869 (m), 2854 (m), 1618 (m, val. arom. C=C), 1607 (m), 1592 (m), 1570 (m), 1503 (s), 1476 (s, δ–CH_2), 1442 (m), 1430 (m, δ–CH_3), 1394 (m), 1386 (m), 1319 (m), 1307 (s, val. asymm. S=O), 1280 (s, acetal C–O–C), 1179 (m), 1165 (m), 1150 (m, val C–O), 1136 (vs, val. symm. S=O), 1104 (m), 1087 (m), 1074 (m), 1046 (m), 1030 (m), 1008 (m), 993 (m), 888 (m), 886 (m), 803 (s, 1,3–disubs. phenyl ring), 781 (m), 703 (m, 1,3–disubs. phenyl ring), 676 (m), 649 (m), 571 (m).

MS (EI): *m/z* (%): = 412 (100) [M^+], 368 (3) [M–CH_3CHO^+], 312 (24) [M-$CHCH_2CH(OCH_2)_2^+$], 171 (16) [$C_{10}H_6OHNN^+$], 143 (54) [$C_{10}H_6OH^+$].

EA: $C_{21}H_{20}N_2O_5S$ (412.46): calc. C 61.15 H 4.89 N 6.79
found C 61.21 H 4.95 N 6.71.

3–[3–(2–Hydroxy–naphthalen–1–ylazo) benzensulphonyl] propanal (**44**)



44

1.12 g (4.72 mmol) of the acetal **39** was deprotected according to general procedure 5.2.4. The aldehyde **44** was obtained as orange needles (0.80 g, 4.17, 80 %) after FC ($CHCl_3$/MeOH/*c*–C_6H_{12} - 9/1/4) and recrystallisation from EtOH, m.p. 186 °C.

^{1}H NMR (DMSO–d_6): δ = 15.56 (s, 1 H, Ar–O<u>H</u>), 9.61 (s, 1 H, 19–H), 8.48 (d, $^3J_{5,4}$ = 7.9 Hz, 1 H, 5–H), 8.29 (s, 1 H, 16–H), 8.20 (br. d, $^3J_{14,13}$ = 7.0 Hz, 1 H, 14–H), 7.96 (d, $^3J_{4,3}$ = 9.5 Hz, 1 H, 4–H), 7.78 (m, 2 H, 12–, 13–H), 7.76 (d, $^3J_{8,7}$ = 7.9 Hz, 1 H, 8-H), 7.63 (t, $^3J_{6,7}$ = 7.2 Hz, 1 H, 6-H), 7.48 (t, $^3J_{7,8}$ = 7.2 Hz, 1 H, 7–H), 6.86 (d,

$^3J_{3,4}$ = 9.5 Hz, 1 H, 3–H), 3.73 (t, $^3J_{17,18}$ = 7.0 Hz, 2 H, 17–H), 4.86 (t, $^3J_{18,17}$ = 7.0 Hz, 2 H, 18–H).

^{13}C NMR (DMSO–d_6): δ = 199.3 (d, C–19), 174.3 (s, C–2), 145.2 (s, C–15), 141.5 (d, C–4), 140.0 (s, C–11), 134.6 (s, C–9), 131.0 (d, C–12), 130.0 (s, C–1), 129.4 (d, C–8), 129.1 (d, C-7), 128.0 (s, C-10), 126.5 (d, C–13), 125.6 (d, C–3), 124.6 (d, C–14), 123.2 (d, C–6), 121.6 (d, C–5), 117.4 (d, C–16), 48.3 (t, C–17), 36.0 (t, C–18).

UV/vis (DMSO): λ_{max} (lg ε) = 262 nm (4.16), 300 (4.05), 410 (4.01), 476 (4.22).

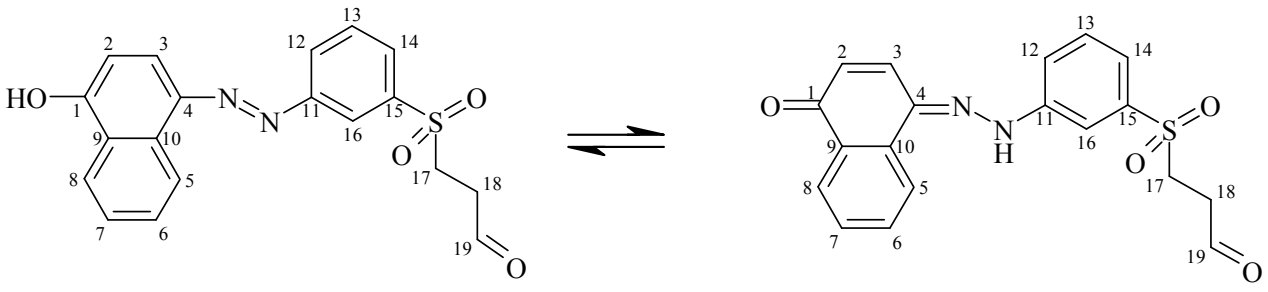
IR[1] (KBr): $\tilde{\nu}$ = 3427 cm^{-1} (s, assoc. ArO–H), 3068 (w), 2986 (w, aliph C–H, CH_3), 2930 (w, aliph C–H, CH_2), 2838 (m, val. asymm. C–HO), 2726 (w, val. symm. C–HO, Fermi`s doublet), 1724 (vs, val. C=O), 1619 (s, val. arom. C=C), 1597 (m), 1561 (m), 1554 (m), 1506 (vs), 1452 (m, δ–CH_2), 1443 (m), 1420 (w, δ–CH_3), 1404 (s), 1385 (m), 1306 (s, val. asymm. S=O), 1277 (m), 1259 (s), 1232 (s), 1209 (vs), 1171 (s), 1155 (s, val. C–O), 1137 (vs, val. symm. S=O), 1073 (m), 995 (m), 987 (m), 904 (w), 865 (m), 842 (s), 787 (s, 1,3–disubs. phenyl ring), 765 (m), 756 (s), 705 (s, 1,3–disubs. phenyl ring), 677 (s), 592 (m), 586 (s), 568 (m).

MS (EI): *m/z* (%): = 368 (97.0) [M^+], 312 (5.6) [M–$C_2H_5CHO^+$], 171 (38.3) [$C_{10}H_6OHNN^+$], 143 (100) [$C_{10}H_6OH^+$].

EA: $C_{19}H_{16}N_2O_4S$ (368.41): calc. C 61.94 H 4.38 N 7.60

found C 61.75 H 4.48 N 7.27.

3–[3–(4–Hydroxy–naphthalen–1–ylazo) benzenesulphonyl] propanal (**45**)



45

Deprotection of 0.74 g (1.80 mmol) of acetal **40** by general procedure 5.2.4 and purification of the product by FC $CHCl_3$/MeOH/*c*–C_6H_{12} (9/1/4), followed by recrystallisation from EtOH yielded aldehyde **45** as orange needles (0.45 g, 1.22 mmol, 68 %), m.p. 172 °C.

^{1}H NMR (DMSO–d_6): δ = 11.80 (br. d, 1 H, Ar–OH), 9.61 (s, 1 H, 19–H), 8.90 (br.s, 1 H, 8–H), 8.32 (m, 2 H, 5–, 16–H), 8.15 (m, 3 H, 3–, 12–, 14–H), 7.78 (m, 2 H, 13–, 7–H), 7.60 (br. s, 1 H, 6–H), 7.05 (br. s, 1 H, 2–H), 3.88 (br.s, 2 H, 17–H), 4.86 (t, $^3J_{18,17}$ = 7.0 Hz, 2 H, 18–H).

^{13}C NMR (DMSO–d_6): δ = 199.3 (d, C–19), 139.8 (d, C–3), 130.9 (d, C–12, –13), 124.6 (d, C–5), 48.4 (t, C–17), 36.1 (t, C–18).

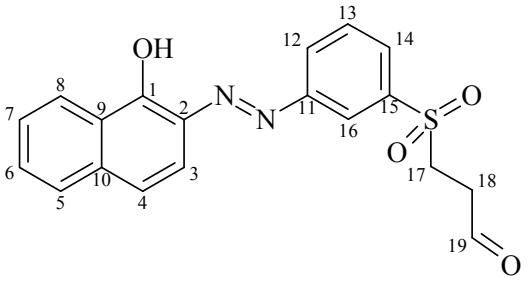
UV/vis (DMSO): λ_{max} (lg ε) = 254 nm (4.12), 280 (4.19), 448 (4.28).

IR[1] (KBr): $\tilde{\nu}$ = 3442 cm^{-1} (s, assoc. ArO–H), 3243 (s), 3213 (s), 3187 (s), 3123 (s), 3060 (s, val. arom. C–H), 3009 (s), 2962 (s, val. aliph. C–H, CH_3), 2921 (s), 2893 (s, val. aliph. C–H, CH_2), 2847 (m, val. asymm. C–HO), 2718 (m, val. symm. C–HO, Fermi`s doublet), 1720 (s, val. CH=O), 1620 (vs, val. arom. C=C), 1596 (vs), 1539 (vs), 1485 (s), 1469 (vs), 1451 (vs), 1412 (vs), 1352 (s), 1307 (vs, val. asymm. S=O), 1272 (vs), 1255 (vs), 1173 (vs), 1139 (vs, val. symm. S=O), 1091 (s), 1073 (s), 1045 (vs), 1013 (vs), 939 (s), 885 (s), 881 (s), 823 (s), 787 (s), 766 (vs), 707 (s, 1,3–disubs. phenyl ring), 684 (s), 559 (s), 551 (s), 500 (vs).

MS (EI): *m/z* (%): = 368 (78) [M^+], 312 (4) [M–$C_2H_5CHO^+$], 248 (19) [M–$SO_2C_2H_4CO^+$], 197 (37) [M–$C_{10}H_6OHNN^+$], 171 (26) [$C_{10}H_6OHNN^+$], 157 (73) [$C_{10}H_6OHNH_2^+$], 143 (100) [$C_{10}H_6OH^+$].

EA: $C_{19}H_{16}N_2O_4S$ (368.41): calc. C 61.94 H 4.38 N 7.60
found C 61.62 H 4.52 N 7.68.

3–[3–(1–Hydroxy–naphthalen–2–ylazo) benzenesulphonyl] propanal (**46**)



46

Cleavage of 0.15 g (0.36 mmol) of acetal **41** according to general procedure 5.2.4 and further purification by FC $CHCl_3$/MeOH/*c*–C_6H_{12} (9/1/4) and recrystallisation from EtOH gave the aldehyde **46** as orange needles (0.10 g, 0.27 mmol, 75 %), m.p. 201–202 °C.

^{1}H NMR (DMSO–d_6): δ = 14.35 (br. s, 1 H, Ar–OH), 9.60 (s, 1 H, 19–H), 8.36 (s, 1 H, 16-H), 8.35 (d, $^3J_{14,\,13}$ = 7.2 Hz, 1 H, 14–H), 8.18 (d, $^3J_{8,\,7}$ = 7.0 Hz, 1 H, 8–H), 7.80 (m, 2 H, 12–, 13–H), 7.79 (d, $^3J_{5,\,6}$ = 8.0 Hz, 1 H, 5–H), 7.76 (t, $^3J_{6,\,7}$ = 7.0 Hz, 1 H, 6–H), 7.58 (t, $^3J_{7,\,8}$ = 7.0 Hz, 1 H, 7–H), 7.42 (d, $^3J_{3,\,4}$ = 9.2 Hz, 1 H, 3–H), 7.25 (d, $^3J_{4,\,3}$ = 9.2 Hz, 1 H, 4-H), 3.70 (t, $^3J_{17,\,18}$ = 7.2 Hz, 2 H, 17–H), 4.85 (t, $^3J_{18,\,17}$ = 7.2 Hz, 2 H, 18–H).

^{13}C NMR (DMSO–d_6): δ = 199.3 (d, C–19), 175.3 (s, C–1), 146.3 (s, C–15), 140.0 (s, C–11), 136.7 (s, C–10), 133.2 (s, C–2), 134.2 (d, C–12), 130.8 (d, C–3), 128.0 (d, C–7), 126.8 (d, C-13), 126.0 (d, C-4), 125.7 (d, C–14), 124.5 (d, C–5), 123.1 (d, C–8), 121.8 (d, C–6), 117.4 (d, C–16), 103 (s, C–9), 48.3 (t, C–17), 36.0 (t, C–18).

UV/vis (DMSO): λ_{max} (lg ε) = 254 nm (4.06), 292 (4.28), 350 (4.08), 432 (3.97), 488 (4.15).

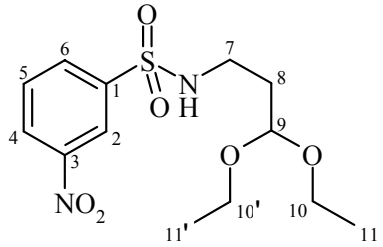
IR[1] (KBr): $\tilde{\nu}$ = 3424 cm^{-1} (w, assoc. ArO–H), 3079 (w, val. arom. C–H), 3060 (w), 2987 (w, val. aliph. C–H, CH_3), 2931 (w, val. aliph. C–H, CH_2), 2916 (w), 2841 (w, val. asymm. C-HO), 2733 (w, val. symm. C–HO, Fermi`s doublet), 1720 (s, val. C=O), 1619 (w), 1610 (m, val. arom. C=C), 1594 (w), 1570 (w), 1506 (vs), 1482 (s), 1442 (m, δ–CH_2), 1430 (w), 1419 (w, δ–CH_3), 1407 (w), 1389 (w), 1323 (m), 1309 (m), 1284 (s, val. as. S=O), 1228 (m), 1218 (m), 1202 (m), 1189 (s), 1168 (m), 1150 (s, val. C–O), 1137 (vs, val. symm S=O), 1088 (w), 1075 (w), 995 (m), 901 (w), 803 (m, 1,3–disubs. phenyl ring), 787 (m), 756 (m), 718 (w), 703 (m, 1,3–disbs. phenyl ring), 679 (m); 587 (m), 574 (w), 564 (m).

MS (EI): *m/z* (%): = 368 (78) [M^+], 312 (7) [$M–C_2H_5CHO^+$], 171 (30) [$C_{10}H_6OHNN^+$], 143 (100) [$C_{10}H_6OH^+$].

EA: $C_{19}H_{16}N_2O_4S$ (368.41): calc. C 61.94 H 4.38 N 7.60
found C 61.77 H 4.74 N 7.74.

5.3.2. Sulphonamidoazo dyes

3–Nitro–*N*–(3,3–diethoxyprop–1–yl) benzenesulphonamide (**29**)



29

5.88 g (40.0 mmol) of 1–amino–3,3–diethoxypropane and 5.00 g (38.8 mmol) of ethyl–diisopropylamine were added to 30 mL of dry acetone in a 250 mL three–necked flask. The solution was stirred under dry nitrogen. In a dropping funnel was placed a solution of 7.13 g (33.0 mmol) of 3–nitrobenzenesulphonyl chloride in 80 mL of acetone, and the solution was added dropwise during 1 h under vigorous stirring. The temperature was held between 30 and 40 °C. The reaction solution was concentrated to $^1/_3$ of its volume under reduced pressure, was then poured into 100 mL of cold water and extracted (2 × 100 mL) with ether. The combined organic phases were washed with water (2 × 50 mL) and dried with $MgSO_4$. The product **29** was obtained after FC (*t*–butylmethylether) 9.60 g (28.9 mmol, 88 %) as a light–yellow oil, which decomposes during attempted distillation (150 °C, 2 mm Hg).

^{1}H NMR ($CDCl_3$): δ = 8.69 (t, $^4J_{2,4}$ = 1.9 Hz, 1 H, 2–H), 8.43 (ddd, $^3J_{6,5}$ = 8.2 Hz, $^4J_{6,2}$ = 4.0 Hz, $^4J_{6,4}$ = 1.0 Hz, 1 H, 6–H), 8.21 (ddd, $^3J_{4,5}$ = 7.9 Hz, $^4J_{4,2}$ = 1.8 Hz, $^4J_{4,6}$ = 1.0 Hz, 1 H, 4–H), 7.78 (t, $^3J_{6,5}$ = 8.0 Hz, 1 H, 4–H), 5.50 (br. s, 1 H, N<u>H</u>), 4.54 (t, $^3J_{9,8}$ = 4.7 Hz, 1 H, 9–H), 3.63 (m, 2 H, 10–H), 3.47 (m, 2 H, 10'–H), 3.18 (t, $^3J_{7,8}$ = 6.2 Hz, 2 H, 7–H), 1.81 (q, $^3J_{8,9}$ = 4.9 Hz, $^3J_{8,7}$ = 6.0 Hz, 2 H, 8–H), 1.17 (t, $^3J_{11,10}$ = 7.0 Hz, 6 H, 11-, 11'–H).

^{13}C NMR (DMSO–d_6): δ = 148.2 (s, C–1), 144.3 (s, C–3), 134.6, 130.4, 126.9, 124.2, 101.1(d, C–9), 64.5 (t, C–10, -10'), 39.1 (t, C–7), 34.4 (t, C–8), 15.2 (q, C–11, –11').

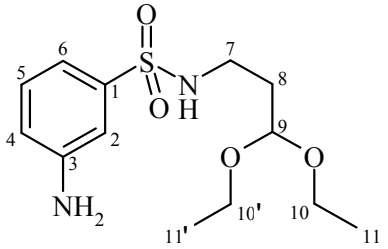
UV/vis ($CHCl_3$): λ_{max} (lg ε) = 242 nm (3.86 sh), 254 (3.89), 336 (2.56).

IR[2] (KBr): $\tilde{\nu}$ = 3293 cm^{-1} (br.w., val. N–H–monosubs. amide), 3091 (w, val. arom. C–H), 2976 (w, val. aliph. C–H, CH_3), 2931 (w, val. aliph. C–H, CH_2), 1607 (w, val. arom. C=C), 1532 (vs, val. SO–NHR, NO_2), 1429 (w, δ–CH_3), 1349 (vs, val. asymm. S=O, NO_2), 1165 (m), 1122 (m, val. C–O), 1051 (vs, val. symm. S=O), 977 (w), 878 (m), 810 (m, 1,3–disubs. phenyl ring), 758 (m), 733 (m), 661(s).

MS (EI): *m/z* (%): = 331 (<0.1) [M–H^+], 303 (<0.1) [M–$C_2H_5^+$], 286 (8) [M–$C_2H_5OH^+$], 215 (23) [M–$CH_2CH(OC_2H_5)_2^+$], 186 (29) [M–$NHC_2H_4CH(OC_2H_5)_2^+$], 103 (81) [$CH(OC_2H_5)_2^+$], 72 (100) [103–CH_3O^+].

EA: $C_{13}H_{20}N_2O_6S$ (332.38): calc. C 46.98 H 6.07 N 8.43
found: C 47.03 H 6.10 N 8.34.

3–Amino–*N*–(3,3–diethoxypropyl) benzenesulphonamide (**30**)



30

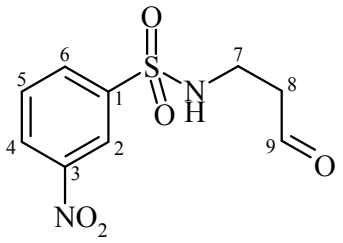
The reduction was carried out analogously to Collins *et al.*[143] 4.19 g (8.77 mmol) of nitro–compound **29** and 125 mg 10 % Pd/C were suspended in 100 mL of EtOH and the mixture placed in a Parr apparatus under H_2 (3.0 atm) for 15 h. After completion of the reaction the catalyst was filtered off and the solvent was removed by distillation. The residue was purified by FC ($CHCl_3$/EtOH/*c*–C_6H_{12} - 9/1/3). The compound **30** was obtained as an yellow oil (1.42 g, 4.70 mmol, 54 %).

^{1}H NMR ($CDCl_3$, 200.13 MHz): δ = 7.27 (d, $^4J_{2,4}$ = 1.4 Hz, 1 H, 2–H), 7.21 (dd, $^4J_{6,2}$ = 1.4 Hz, $^3J_{6,5}$ = 4.7 Hz, 1 H, 6–H), 7.15 (t, $^3J_{5,6}$ = 4.7 Hz, 1 H, 5–H), 6.84 (dd, $^4J_{4,2}$ = 1.4 Hz, $^3J_{4,5}$ = 4.7 Hz, 1 H, 4–H), 5.21 (t, $^3J_{NH,7}$ = 5.9 Hz, 1 H, AlkN<u>H</u>), 4.50 (t,

$^3J_{9,8}$ = 5.2 Hz, 1 H, 9–H), 3.70(m, 6 H, 10–, 10'–, ArNH), 3.05 (q, $^3J_{7,8}$ = 6.2 Hz, $^3J_{7,NH}$ = 6.0 Hz, 2 H, 7–H), 1.75 (q, $^3J_{8,9}$ = 5.2 Hz, $^3J_{8,7}$ = 6.4 Hz, 2 H, 8–H), 1.18 (t, $^3J_{11,10}$ = 7.0 Hz, 6 H, 11–, 11'–H).

MS (EI): *m/z* (%): = 302 (54) [M^+], 273 (6) [$M–C_2H_5^+$], 256 (43) [$M–C_2H_5OH^+$], 185 (56) [$M–CH_2CH(OC_2H_5)_2^+$], 156 (57) [$M–NHC_2H_4CH(OC_2H_5)_2^+$], 103 (100) [$CH(OC_2H_5)_2^+$].

3–Nitro–*N*–(3–oxo–propyl) benzenesulphonamide (**32**)



32

Cleavage of the protecting group of **29** was performed according to general procedure 5.2.4 in methanol. 7.9 g (23.8 mmol) of **29** was dissolved in 30 mL of MeOH and 5 mL of 2 *N* HCl was added. The solution was stirred for 2 h at ambient temperature and 30 min under reflux, cooled to room temperature and poured into 100 mL of water. The organic phase was extracted (2 × 100 mL) with ether, washed (2 × 50 mL) with water and dried with $MgSO_4$. The aldehyde **32** appeared as an oil (5.8 g, 24.5 mmol, 95.0 %) after distillation of the ether and FC C_6H_{14}/EtOAc/EtOH (20/10/1). It crystallised slowly from a small amount of $CHCl_3$ as white prisms, m.p. 100 °C.

^{1}H NMR (acetone–d_6): δ = 9.55 (s, 1 H, H–9), 8.51 (t, $^4J_{2,4}$ = 4.0 Hz, 1 H, 2–H), 8.38 (ddd, $^3J_{6,5}$ = 8.1 Hz, $^4J_{6,2}$ = 4.0 Hz, $^4J_{6,4}$ = 1.0 Hz, 1 H, 6–H), 8.15 (ddd, $^3J_{4,5}$ = 8.1 Hz, $^4J_{4,2}$ = 1.7 Hz, $^4J_{4,6}$ = 1.0 Hz, 1 H, 4–H), 7.82 (t, $^3J_{6,5}$ = 8.1 Hz, 1 H, 4–H), 6.80 (br. s, 1 H, NH), 3.17 (t, $^3J_{7,8}$ = 6.5 Hz, 2 H, 7–H), 4.60 (t, $^3J_{8,7}$ = 6.5 Hz, 2 H, 8–H).

^{13}C NMR (acetone–d_6): δ = 201.0 (d, C–9), 149.3 (s, C–1), 143.4 (s, C–3), 133.6 (d, C–5), 131.9 (d, C–4), 127.8 (d, C–6), 124.7 (d, C–2), 44.1 (t, C–7), 37.6 (t, C–8).

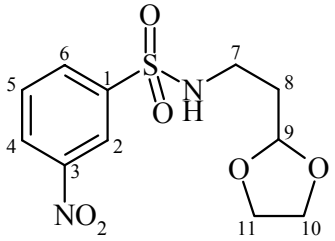
UV/vis ($CHCl_3$): λ_{max} (lg ε) = 322 nm (2.68 sh), 330 (2.83).

IR[2] (KBr): $\tilde{\nu}$ = 3303 cm^{-1} (m, val. N–H–monosubs. amide), 3103 (w, val. arom. C–H), 2933 (w, val. aliph. C–H, CH_3), 2907 (w, val. aliph. C–H, CH_2), 2866 (w, val. asymm. C–HO), 1737 (m, val. C=O), 1702 (m), 1604 (w, val. arom. C=C), 1525 (s, val. assym. NO_2), 1464 (m, δ–CH_2), 1438 (s), 1330 (vs, val. asymm. S=O), 1124 (vs, val. symm. S=O), 1095 (s, val. C–O), 1072 (vs), 975 (m), 864 (m), 838 (m), 819 (s, 1,3–disubs. phenyl ring), 758 (m), 732 (s), 672 (m), 658 (s), 641 (m), 568 (vs), 536 (s).

MS (EI): *m/z* (%): = 258 (<0.1) [M^+], 241 (6) [M–OH^+], 230 (34) [M–CO^+], 215 (18) [M-$CHCO^+$], 202 (24) [M–$C_2H_4CO^+$], 186 (70) [M–$C_3H_7CHO^+$], 122 (100) [$C_6H_4NO_2^+$].

EA: $C_9H_{10}N_2O_5S$ (258.24): calc. C 41.86 H 3.90 N 10.85
found: C 41.41 H 3.90 N 10.47.

3–Nitro–*N*–(2–[1,3] dioxolan–yl–ethyl) benzenesulphonamide (**26**)



26

5.40 g (20.9 mmol) of aldehyde **32**, 4.00 g (30.3 mmol) of 1,2–ethanediol and 1.00 g of Amberlite 15 were mixed in 10 mL of dry THF according to Dann *et al*.[72]. The mixture was stirred for 3 h at ambient temperature and 2 h at 60 °C. After cooling, the resin was filtered off and the filtrate was poured into 150 mL of water. The organic phase was extracted (2 × 100 mL) with ether, washed with water (2 × 50 mL) and dried with $MgSO_4$. The ether solution was distilled and the residue was chromatographed (*t*–butylmethylether). Acetal **26** was obtained as heavy pale–yellow oil (4.30 g, 14.2 mmol, 68 %).

^{1}H NMR ($CDCl_3$): δ = 8.70 (t, $^4J_{2,4}$ = 1.9 Hz, 1 H, 2–H), 8.43 (dd, $^3J_{6,5}$ = 8.1 Hz, $^4J_{6,2}$ = 1.9 Hz, 1 H, 6–H), 8.21 (dd, $^3J_{4,5}$ = 8.1 Hz, $^4J_{4,2}$ = 1.9 Hz, 1 H, 4–H), 7.78 (t, $^3J_{6,5}$ = 8.1 Hz, 1 H, 4–H), 5.58 (br. s, 1 H, NH), 4.85 (t, $^3J_{9,8}$ = 4.0 Hz, 1 H, 9–H), 3.88 (m, AA'BB', 4 H, 10–, 11–H), 3.18(q, $^3J_{7,NH}$ = 5.9 Hz, $^3J_{7,8}$ = 5.8 Hz, 2 H, 7–H), 1.88 (q, $^3J_{8,9}$ = 4.1 Hz, $^3J_{8,7}$ = 5.9 Hz, 2 H, 8–H).

^{13}C NMR ($CDCl_3$): δ = 148.3 (s, C–1), 144.4 (s, C–3), 134.6 (d, C–5), 130.5 (d, C–4), 127.0 (d, C–6), 124.2 (d, C–2), 103.0 (d, C–9), 64.9 (t, C–10, –11), 38.5 (t, C–7), 31.9 (t, C–8).

UV/vis ($CHCl_3$): λ_{max} (lg ε) = 244 nm (3.88 sh), 254 (3.89), 328 (2.72).

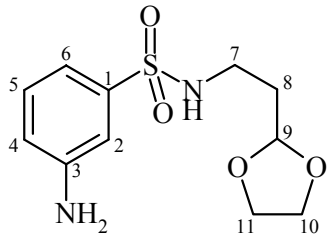
IR[2] (KBr): $\tilde{\nu}$ = 3289 cm^{-1} (m, val. N–H–monosubs. amide), 3081 (m, val. arom. C–H), 2889 (w, val. aliph. C–H, CH_2), 1604 (w, val. arom. C=C), 1528 (s, val. assym. NO_2), 1436 (s), 1330 (s, val. assym. S=O), 1275 (m, acetal C–O–C,), 1231 (w), 1161 (s), 1123 (s, val. symm. S=O), 1086 (s, val. C–O), 1066 (s), 1014 (s), 945 (m), 879 (m), 843 (m), 821 (m), 736 (m), 659 (s), 574 (s).

MS (CI/DCI pos.): *m/z* (%): = 320 (40) [$M+NH_4^+$], 290 (90) [$M_{(320)}$–$HCHO^+$], 275 (24), [$M_{(320)}$.$C_2H_4CHO^+$], 118 (100) [$NH_3C_2H_4CH(OCH_2)_2^+$].

MS (EI): *m/z* (%): = 301 (< 0.1) [$M–H^+$], 215 (4) [$M–CH_2CH(OCH_2)_2^+$], 186 (8) [$M-NHC_2H_4CH(OCH_2)_2^+$], 73 (100) [$CH(OCH_2)_2^+$].

EA: $C_{11}H_{14}N_2O_6S$ (302.34): calc. C 43.70 H 4.67 N 9.27
found: C 43.66 H 4.73 N 9.15.

3–Amino–*N*– (2–[1,3] dioxolan–yl–ethyl) benzenesulphonamide (**34**)



34

The synthesis of compound **34** was performed as described above for **30**. 4.30 g (7.62 mmol) of **26** was dissolved in 100 mL of EtOH and 250 mg of Pd/C (10 %) was added. The mixture was poured into a Parr apparatus and was placed under H_2 (3.0 bar) for 3 h. The catalyst was filtered off and EtOH was removed by distillation. The aniline **34** was obtained as a light yellow oil (4.00 g, 7.35 mmol, 96 %).

^{1}H NMR (acetone–d_6): δ = 7.26 (t, $^3J_{5,6}$ = 7.9 Hz, 1 H, 5–H), 7.15 (t, $^4J_{2,4}$ = 1.7 Hz, 1 H, 2-H), 7.05 (br.d, $^3J_{6,5}$ = 7.9 Hz, 1 H, 6–H), 6.90 (dd, $^4J_{4,2}$ = 1.6 Hz, $^3J_{4,5}$ = 7.9 Hz, 1 H, 4–H), 6.14 (br.s, 1 H, $SO_2N\underline{H}$), 5.11 (br.s, 2 H, Ar$N\underline{H}$), 4.85 (t, $^3J_{9,8}$ = 4.5 Hz, 1 H, 9–H), 3.84 (m, AA'BB', 4 H, 10–, 11–H), 3.04 (q, $^3J_{7,NH}$ = 6.4 Hz, $^3J_{7,8}$ = 6.9 Hz, 2 H, 7–H), 1.83 (m, 2 H, 8-H).

^{13}C NMR (acetone–d_6): δ = 150.1 (s, C–3), 144.2 (s, C–1), 130.4 (d, C–5), 118.5 (d, C–6), 115.4 (d, C–4), 114.8 (d, C–2), 103.1 (d, C–9), 65.4 (t, C–10, –11), 39.4 (t, C–7), 34.2 (t, C-8).

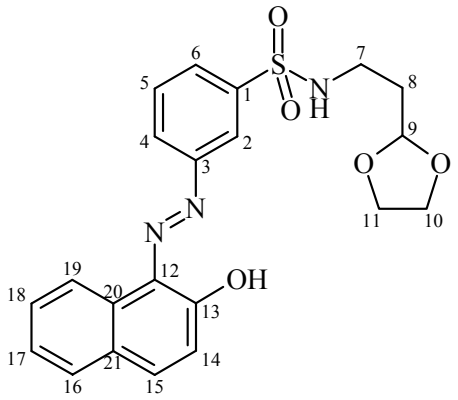
UV/vis (acetone): λ_{max} (lg ε) = 328 nm (3.01).

IR[2] (KBr): $\tilde{\nu}$ = 3467 cm^{-1} (w, val. Ar$\underline{NH_2}$), 3371 (w, val. Ar$\underline{NH_2}$), 3252 (br.w, val. N–H–monosubs. amide), 2959 (w), 2932 (w, val. aliph. C–H, CH_3), 2887 (w, val. aliph. C–H, CH_2), 1705 (w), 1627 (m, val. arom. C=C), 1598 (s), 1483 (m), 1452 (m, δ–CH_2), 1416 (w, δ–CH_3), 1307 (vs, val. assym. S=O), 1276 (m, acetal C–O–C), 1227 (vs), 1147 (vs, val. symm. S=O), 1080 (s, val. C–O), 1025 (m), 991 (w), 943 (w), 900 (w), 866 (w), 781 (m, 1,3–disubs. phenyl ring), 753 (w), 701(m, 1,3–disubs. phenyl ring), 684 (m), 614 (w), 582 (vs), 532 (m).

MS (EI): *m/z* (%): = 272 (4) [M^+], 165 (27), 92 (36) [$C_6H_5NH^+$], 87 (64) [$CH_2CH(OCH_2)_2^+$], 73 (100) [$CH(OCH_2)_2^+$].

EA: $C_{11}H_{16}N_2O_4S$ (272.30): calc. C48.52 H 5.92 N 10.29
found: C 48.97 H 6.08 N 10.17.

N– (2–[1,3] dioxolan–yl–ethyl)–3–(2–hydroxynaphthalen–1–ylazo) benzenesulphonamide (**31a**)



31a

According to general procedure 5.2.1 0.83 g (3.00 mmol) of aniline **34** was diazotised and was coupled with 0.41 g (3.00 mmol) of 2–naphthol. Purification by FC $CHCl_3$/c–C_6H_{12}/EtOAc (5/3/2) and recrystallisation from acetone–water provided the dye **31a** as orange needles (0.55 g, 1.34 mmol, 70 %), m.p. 195 °C.

^{1}H NMR (DMSO–d_6): δ = 15.62 (br. s, 1 H, ArO<u>H</u>), 8.49 (d, $^3J_{16,17}$ = 8.1 Hz, 1 H, 16–H), 8.21 (t, $^4J_{2,6}$ = 1.7 Hz, 1 H, 2–H), 8.08 (dt, $^3J_{6,5}$ = 7.1 Hz, $^4J_{6,2}$ = 1.7 Hz, 1 H, 6–H), 7.96 (d, $^3J_{15,14}$ = 9.5 Hz, 1 H, 15–H), 7.85 (br. s, 1 H, N<u>H</u>), 7.79 (m, 3 H, 4–, 5–, 19–H), 7.64 (td, $^3J_{17,18}$ = 8.1 Hz, $^4J_{17,19}$ = 1.2 Hz, 1–H, 17–H), 7.50 (td, $^3J_{18,17}$ =8.1 Hz, $^4J_{18,16}$ = 1.1 Hz, 1–H, 18–H), 6.88 (d, $^3J_{14,13}$ =9.5 Hz, 1–H, 14–H), 4.80 (t, $^3J_{9,8}$ =4.7 Hz, 1–H, 9–H), 3.75 (m, AA'BB', 4–H, 10–, 11–H), 4.92 (t, $^3J_{7,8}$ =7.2 Hz, 2–H, 7–H), 1.74 (dt, $^3J_{8,9}$ =4.7 Hz, $^3J_{8,7}$ =7.2 Hz, 2–H, 8–H).

^{13}C NMR (DMSO–d_6): δ = 171.8 (s, C–13), 145.1 (d, C–15), 141.9 (s, C–1), 141.2 (s, C–3), 134.6 (d, C–4), 130.8 (d, C–17), 129.8 (s, C–20), 129.4 (s, C–12), 129.1 (s, C–21), 128.0 (d, C–19), 126.4 (d, C–18), 124.7 (s, C–5), 124.5 (d, C–14), 124.4 (d, C–6), 121.4 (d, C–16), 115.6 (d, C–2), 101.3 (d, C-9), 64.2 (t, C–10, –11), 39.5 (t, C–7), 33.4 (t, C–8).

UV/vis (DMSO): λ_{max} (lg ε) = 262 nm (4.59), 278 (4.56 sh), 414 (4.02 sh), 454 (4.13), 502 (4.12 sh).

UV/vis (1,4–dioxane): λ_{max} (lg ε) = 232 nm (4.62), 266 (4.12 sh), 304 (3.93), 420 (4.07 sh), 474 (4.22), 500 (4.13 sh).

UV/vis (EtOH): λ_{max} (lg ε) = 210 nm (4.55 sh), 228 (4.63), 262 (4.07), 302 (3.93), 418 (4.08 sh), 474 (4.23).

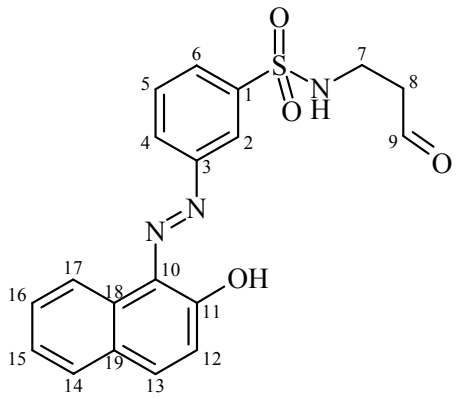
UV/vis ($CHCl_3$): λ_{max} (lg ε) = 242 nm (4.32), 258 (4.09 sh), 304 (3.95), 422 (4.05 sh), 478 (4.26).

IR[1] (KBr): $\tilde{\nu}$ = 3279 cm^{-1} (s, val. N–H–monosubs. amide), 3050 (w, val. arom. C–H), 2982 (w), 2960 (w, val. aliph. C–H, CH_3), 2934(w), 2888 (w, val. aliph. C–H, CH_2), 2856 (w), 1619 (w, val. arom. C=C), 1565 (w), 1500 (m), 1475 (s), 1450 (m, δ– CH_2), 1440 (s), 1388 (m), 1332 (vs, val. asymm. S=O), 1312 (m), 1277 (w), 1253 (m, acetal C–O–C), 1206 (s), 1158 (vs, val. symm. S=O), 1134 (s, val. C–O), 1087 (w), 1074 (m), 1014 (w), 994 (w), 918 (w), 863 (w), 793 (m, 1,3–disubs. phenyl ring), 704 (m, 1,3–disubs. phenyl ring), 680 (m), 642 (m), 578 (m), 512 (m).

MS (EI): *m/z* (%): = 427 (58) [M^+], 339 (14) [M–$CH_3CH(OCH_2)_2^+$], 270 (7), [M-$C_{10}H_6OHN^+$], 171 (36) [$C_{10}H_6OHNN^+$], 143 (100) [$C_{10}H_6OH^+$].

EA: $C_{21}H_{21}N_3O_5S$ (427.51): calc. C 59.00 H 4.95 N 9.83
found: C 58.91 H 4.95 N 9.81.

3–(2–hydroxynaphthalen–1–ylazo)–*N*–(3–oxo–propyl) benzenesulphonamide (**47**)



47

Cleavage of the protecting group was performed according to general procedure 5.2.4, as solvent a mixture of DMF (20 mL) and acetone (30 mL) was used. 1.85 g (4.33 mmol) of acetal **31a** was dissolved in the solvent mixture. 10 mL of 10 % H_2SO_4 was added and the reaction solution was stirred for 4 h at 75 °C. The solution was cooled to room temperature and poured into 200 mL of ice–water, stirred for 2 h and filtered. The solid was

chromatographed (EtOAc/C_6H_{14} - 1/2) and recrystallised from *i*–PrOH. The aldehyde **47** forms dark–orange plates, which change to needles at 115–120 °C (1.40 g, 3.65 mmol, 84 %) m.p. 180–182 °C.

^{1}H NMR (DMSO–d_6): δ = 15.62 (br. s, 1 H, ArO<u>H</u>), 9.60 (t, $^3J_{9,8}$ = 1.3 Hz, 1–H, 9–H), 8.50 (d, $^3J_{14,15}$ = 8.1 Hz, 1-H, 14–H), 8.22 (d, $^4J_{2,6}$ = 1.7 Hz, 1–H, 2–H), 8.10 (dt, $^3J_{6,5}$ = 7.0 Hz, $^3J_{6,2}$ = 1.7 Hz, 1 H, 6–H), 7.97 (d, $^3J_{13,12}$ = 9.5 Hz, 1–H, 13–H), 7.75 (m, 3–H, 4–, 5–, 17–H), 7.65 (td, $^3J_{15,16}$ = 8.1 Hz, $^4J_{15,17}$ = 1.1 Hz, 1–H, 15–H), 7.50 (dt, $^3J_{16,17}$ = 8.1 Hz, $^4J_{16,14}$ = 1.1 Hz, 1–H, 16–H), 6.89 (d, $^3J_{12,13}$ = 9.5 Hz, 1–H, 12–H), 3.13 (t, $^3J_{8,7}$ = 6.7 Hz, 2-H, 7–H), 4.62 (td, $^3J_{8,7}$ = 6.7 Hz, $^3J_{8,9}$ = 1.3 Hz, 2–H, 8–H).

^{13}C NMR (DMSO–d_6): δ = 201.7 (d, C–9), 171.8 (s, C–11), 145.2 (s, C–1), 141.7 (s, C–3), 141.3 (d, C–13), 134.6 (s, C–18), 130.8 (d, C–4), 129.8 (s, C–19), 129.4 (d, C–17), 129.1 (s, C–10), 128.0 (d, C–15), 126.5 (d, C–16), 124.7 (d, C–5), 124.5 (d, C–12), 124.4 (d, C–6), 121.5 (d, C–14). 115.7 (d, C–2), 44.8 (t, C–7), 36.5 (t, C–8).

UV/vis (DMSO): λ_{max} (lg ε) = 262 nm (4.39), 428 (4.06 sh), 478 (4.20), 506 (4.08 sh).

UV/vis (1,4–dioxane): λ_{max} (lg ε) = 232 nm (4.54), 262 (4.05), 304 (3.91), 418 (4.04 sh), 474 (4.21), 500 (4.10 sh).

UV/vis (EtOH): λ_{max} (lg ε) = 210 nm (4.48 sh), 228 (4.57), 262 (4.01), 302 (3.88), 428 (4.05 sh), 474 (4.17), 500 (4.07 sh).

UV/vis ($CHCl_3$): λ_{max} (lg ε) = 242 nm (4.27), 258 (4.07 sh), 304 (3.94), 420 (4.01 sh), 478 (4.24).

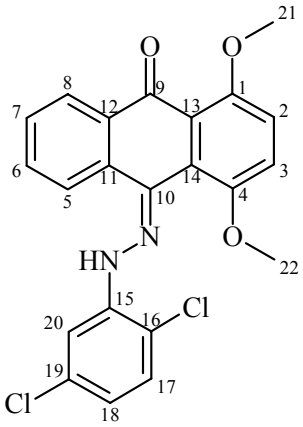
IR[2] (KBr): $\tilde{\nu}$ = 3293 cm^{-1} (w, val. N–H–monosubs. amide), 3065 (w, val. arom. C–H), 2868 (w, val. aliph. C–H, CH_3), 1720 (m, val. C=O), 1617 (m, val. arom. C=C), 1597 (w), 1559(w), 1500 (vs), 1443(m, δ–CH_2), 1400 (w), 1329 (s, val. asymm. S=O), 1311 (s), 1256 (m), 1228 (m), 1208 (w), 1153 (vs, val. symmm. S=O), 1079 (m, val. C–O), 986 (m), 863 (w), 834 (w), 788 (m, 1,3–disbus. phenyl ring), 752 (m), 700 (m, 1,3–disbus. phenyl ring), 678 (m), 653 (m), 583 (vs), 546 (w).

MS (EI): *m/z* (%): = 383 (45) [M^+], 327 (27) [$M–C_2H_4CO^+$], 246 (19) [$M\text{-}SO_2NHC_2H_4CHOH^+$], 171 (35) [$C_{10}H_6OHNN^+$], 143 (100) [$C_{10}H_6OH^+$].

EA: $C_{19}H_{17}N_3O_4S$ (383.42): calc. C 59.52 H 4.47 N 10.96
found: C 59.13 H 4.70 N 10.66.

5.3.3. Anthraquinone monophenylhydrazone dyes

10–[(2,5–Dichlorophenyl)–hydrazono] 1,4–dimethoxyanthracen–9–one (**60**)



60

Compound **60** was obtained analogously to the procedure given in reference.[83] 2.25 g (8.40 mmol) of 1,4-dimethoxyantraquinone **58** and 1.49 g (8.40 mmol) of 2,5–dichlorophenylhydrazine **59** were dissolved in 60 mL of EtOH and 15 mL of 60 % acetic acid was poured into the solution. The reaction mixture was refluxed for 4 h, stirred overnight at ambient temperature and then poured into 200 mL of water. The solid was filtered off and purified by FC CH_2Cl_2/EtOAc (8/1) and recrystallised from EtOH: yellow needles (2.10 g, 4.92 mmol, 58 %), m.p. 170 °C.

^{1}H NMR (acetone–d_6): δ = 9.47 (s, 1 H, N<u>H</u>), 7.96 (ddd, $^5J_{8,5}$ = 0.5 Hz, $^4J_{8,6}$ = 1.2 Hz, $^3J_{8,7}$ = 7.8 Hz, 1 H, 8–H), 7.81 (ddd, $^5J_{5,8}$ = 0.4 Hz, $^4J_{5,7}$ = 1.2 Hz, $^3J_{5,6}$ = 7.8 Hz, 1 H, 5–H), 7.56 (td, $^4J_{7,5}$ = 1.2 Hz, $^3J_{7,8}$ = 7.8 Hz, 1 H, 7–H), 7.48 (d, $^4J_{20,18}$ = 2.4 Hz, 1 H, 20–H), 7.47 (d, $^3J_{17,18}$ = 8.1 Hz, 1 H, 17–H), 7.41 (td, $^4J_{6,8}$ = 1.2 Hz, $^3J_{6,5}$ = 7.8 Hz, 1 H, 6–H), 7.31 (d, $^3J_{2,3}$ = 9.4 Hz, 1 H, 2–H), 7.24 (d, $^3J_{3,2}$ = 9.4 Hz, 1 H, 3–H), 6.78 (dd, $^4J_{18,20}$ = 2.4 Hz, $^3J_{18,17}$ = 8.4 Hz, 1 H, 18–H), 4.00 (s, 3 H, 21–H), 3.80 (s, 3 H, 22–H).

^{13}C NMR (DMSO–d_6): δ = 206.4 (s, C–9), 183.3 (s, C–10), 155.4 (s, C–1), 149.2 (s, C–4), 142.9 (s, C–15), 139.3 (s, C–12), 136.8 (s, C–11), 134.6 (s, C–13), 134.4 (s, C–19), 133.2 (d, C–7), 131.4 (d, C–17), 129.1 (d, C–6), 126.3 (d, C–5), 125.3 (d, C–8), 123.1 (s, C–13), 122.6 (s, C–14), 121.5 (d, C-18), 119.0 (d, C–2), 117.8 (d, C–3), 117.2 (s, C–16), 114.8 (d, C–20), 57.7 (q, C–21), 57.3 (q, C–22).

^{1}H NMR ($CDCl_3$): δ = 9.38 (s, 1 H, NH), 7.99 (d, $^{3}J_{8,7}$ = 8.2 Hz, 2 H, 8–, 5–H), 7.56 (d, $^{4}J_{20,18}$ = 2.5 Hz, 1 H, 20–H), 7.55 (td, $^{4}J_{7,5}$ = 1.1 Hz, $^{3}J_{7,8}$ = 7.8 Hz, 1 H, 7–H), 7.40 (td, $^{4}J_{6,8}$ = 1.2 Hz, $^{3}J_{6,5}$ = 7.8 Hz, 1 H, 6–H), 7.23 (d, $^{3}J_{2,3}$ = 9.3 Hz, 1 H, 2–H), 7.15 (d, $^{3}J_{3,2}$ = 9.3 Hz, 1 H, 3-H), 7.14 (d, $^{3}J_{17,18}$ = 8.5 Hz, 1 H, 17–H), 6.72 (dd, $^{4}J_{18,20}$ = 2.5 Hz, $^{3}J_{18,17}$ = 8.5 Hz, 1 H, 18–H), 3.94 (s, 3 H, 21–H), 3.91 (s, 3 H, 22–H).

^{13}C NMR ($CDCl_3$): δ = 183.9 (s, C–9), 154.7 (s, C–10), 148.1 (s, C–1), 141.6 (s, C–4), 138.6 (s, C–15), 134.8 (s, C–12), 134.1 (s, C–11), 133.2 (s, C–19), 132.4 (d, C–7), 129.9 (d, C–17), 128.1 (d, C–6), 126.0 (d, C–5), 124.4 (d, C–8), 122.6 (s, C–13), 122.5 (s, C–14), 120.7 (d, C-18), 117.5 (d, C–2), 116.2 (s, C–16), 115.6 (d, C–3), 114.5 (d, C–20), 57.1 (q, C–21), 57.09 (q, C–22).

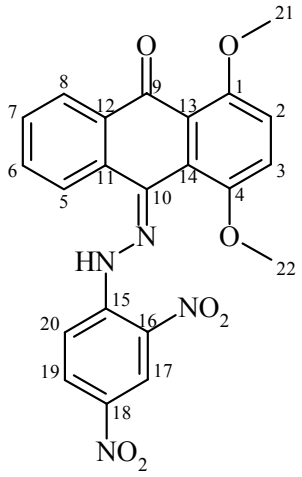
UV/vis (DMSO): λ_{max} (lg ε) = 262 nm (4.26), 330 (3.97), 392 (4.15), 414 (4.18).

IR[2] (KBr): $\tilde{\nu}$ = 3250 cm^{-1} (w, val. ArNH), 3091 (w, val. arom. C–H), 3029 (w), 2953 (w, val. aliph. C-H, CH_3), 2929 (w), 2829 (w), 1657 (vs, val. C=O), 1584 (vs, val. arom. C=C), 1537 (s), 1497 (s), 1470 (m), 1450 (m), 1413 (m, δ– CH_3), 1324 (m), 1309 (vs), 1271 (vs, val. C-O), 1207 (m), 1187 (m), 1075 (s, val. C–O–C), 1056 (s), 1043 (s), 978 (s), 950 (m), 873 (m), 858 (m), 811 (m, two neighbours arom. H–atoms), 764 (s, 4 neighbours arom. H–atoms), 702 (m).

MS (EI): *m/z* (%): = 428 (62), [M^+], 395 (41) [M–CH_3O^+].

EA: $C_{22}H_{16}Cl_2N_2O_3$ (427.29):	calc.	C 61.84 H 3.77 N 6.56 Cl 16.59
	found:	C 61.44 H 3.82 N 6.51 Cl 16.46.

10–[(2,4–Dinitrophenyl)–hydrazono] 1,4–dimethoxyanthracen–9–one (**62**)



62

The dye **62** was synthesised analogously to the procedure described in reference.[84] 1.60 g (5.97 mmol) of 1,4-dimethoxyanthraquinone **58** and 1.18 g (6.0 mmol) of 1.4–dinitrophenylhydrazine **61** were dissolved in 50 mL of ethanol and 5 mL of 2 *N* HCl was added to the solution. The reaction was heated for 5 h under reflux and filtered while hot. On cooling, crystals appeared, which were collected by filtration. The crude product was 3 times recrystallised from DMF. Derivative **62** was obtained as red needles (1.65 g, 3.68 mmol, 61 %), m.p. 266 °C.

^{1}H NMR (DMSO–d_6): δ = 11.49 (s, 1 H, NH), 8.91 (d, $^4J_{17,19}$ = 2.6 Hz, 1 H, 17–H), 8.44 (dd, $^4J_{19,17}$ = 2.6 Hz, $^3J_{19,20}$ = 6.9 Hz, 1 H, 19–H), 8.14 (d, $^3J_{8,7}$ = 9.8 Hz, 1 H, 8–H), 8.11 (d, $^3J_{5,6}$ = 9.3 Hz, 1 H, 5–H), 7.94 (dd, $^4J_{20,17}$ = 0.8 Hz, $^3J_{20,19}$ = 7.0 Hz, 1 H, 20–H), 7.76 (td, $^4J_{6,8}$ = 1.3 Hz, $^3J_{6,5}$ = 7.5 Hz, 1 H, 6–H), 7.67 (d, $^3J_{2,3}$ = 9.4 Hz, 1 H, 2–H), 7.64 (td, $^4J_{7,5}$ = 1.3 Hz, $^3J_{7,8}$ = 7.6 Hz, 1 H, 7–H), 7.54 (d, $^3J_{3,2}$ = 9.4 Hz, 1 H, 3–H), 4.00 (s, 3 H, 21-H), 3.93 (s, 3 H, 22–H).

^{13}C NMR (DMSO–d_6): δ = 181.5 (s, C–9), 153.5 (s, C–10), 148.2 (s, C–1, –16), 141.7 (s, C-4, –18), 136.6 (s, C–15), 132.9 (s, C–12, –11), 132.2 (d, C–7), 129.5 (d, C–19), 129.0 (d, C–6), 125.2 (d, C–5), 123.9 (d, C–8), 122.3 (d, C–20), 121.4 (s, C–13, –14), 118.5 (d, C–2), 118.1 (d, C–3), 116.5 (d, C-17), 56.8 (q, C–21), 56.2 (q, C–22).

UV/vis (DMSO): λ_{max} (lg ε) = 264 nm (4.43), 400 (4.45), 445 (4.35 sh).

UV/vis (EtOH): λ_{max} (lg ε) = 214 nm (4.45), 236 (4.42), 392 (4.36), 436 (4.23 sh).

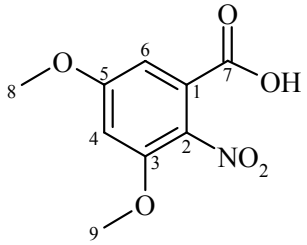
IR[2] (KBr): $\tilde{\nu}$ = 3232 cm^{-1} (m, val. Ar<u>NH</u>), 3101 (w, val. arom. C–H), 3064 (w), 2961 (w, val. aliph. C–H, CH_3), 2936 (w), 2831 (w), 1661 (vs, val. C=O), 1611 (vs (val. C=N), 1587 (vs, val. asymm. C–NO_2), 1512 (s, δ–CH_3), 1491 (s), 1448 (m), 1414 (m), 1393 (s), 1313 (vs, val. symm. C–NO_2), 1274 (s), 1251 (m), 1197 (vs, val. C–O), 1071 (s, val. C–O–C), 1040 (s), 974 (vs), 936 (m), 909 (m), 847 (m), 814 (m, 2 neighbours arom. H–atoms); 768 (s, 4 neighbours arom. H–atoms), 726 (m), 701 (m), 682 (m).

MS (EI): *m/z* (%): = 448 (46), [M^+], 431 (14) [M–OH^+], 417 (100), [M–CH_3O^+], 400 (5) [$K_{(431)}$–CH_3O^+], 371 (8.1), [$K_{(417)}$–NO_2^+].

EA: $C_{22}H_{16}N_4O_7$ (448.40):	calc.	C 58.93, H 3.60, N 12.49
	found:	C 58.53, H 3.56, N 12.49.

5.4. 9–(10–H) acridones–and acridines

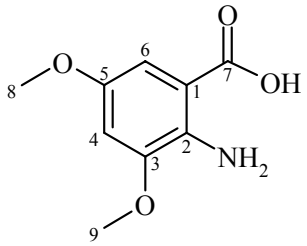
3,5–Dimethoxy–2–nitrobenzoic acid (**64**)



64

Compound **64** was prepared according to Insole.[86] 6.07 g (30.00 mmol) of 3,5-dimethoxybenzoic acid **63** was dissolved in 10 mL of acetic acid. A solution of 1 mL conc. HNO_3 in 15 mL of acetic anhydride was added to the solution. The temperature was increased to 70 °C for 10 min and was kept for the next 2 h at 50 °C. After cooling, the product precipitated and the mixture was poured into 100 mL of ice–water. The solid was filtered off and recrystallised from EtOH. Compound **64** appeared as light–yellow needles (6.45 g, 28.40 mmol, 94 %), m.p. 235 °C (lit.[143]: 232°C).

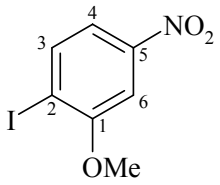
3,5–Dimethoxyanthranilic acid (**65**)



65

The reduction of compound **64** was performed by catalytic hydrogenation with 10 % Pd/C as the catalyst. The yield was much better than given in the literature.[92] 6.82 g (30.00 mmol) of reagent **64** was dissolved in 300 mL of EtOH and 0.24 g 10 % Pd/C was added. The suspension was placed in a Parr apparatus at 3.0 atm of H_2 for 16 h. The catalyst was filtered off and the solvent was removed by distillation. The aniline **65** crystallised as light–yellow plates (5.41 g, 27.40 mmol, 91 %, ref.[86]: 69 %), m.p. 168 °C (ref.[92]: 170–177).

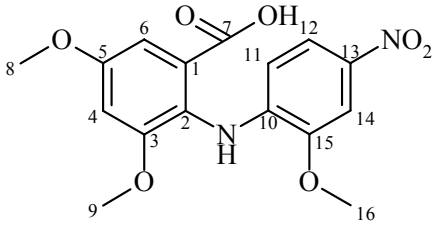
2–Iodo–5–nitro–methoxybenzene (**67**)



67

The preparation of compound **67** was carried out according to Hanford and Adams[91]: 1.90 g (11.30 mmol) of 2–methoxy–4–nitroaniline **66** was dissolved in 25 mL of 30 % H_2SO_4. The solution was cooled to 0 °C and 3.3 mL of 25 % aqueous solution of $NaNO_2$ was added dropwise during 10 min. After 1 h at 0–5 °C the reaction was quenched and the reaction mixture was filtered. To the filtrate was poured in one portion a solution of 2.00 g (12.0 mmol) KI in 2.5 mL of water. After the evolution of nitrogen had stopped, the suspension was boiled for 1 h, cooled and the solid was filtered off. Compound **67** was obtained by recrystallisation from EtOH as brown–yellow needles (2.94 g, 10.8 mmol, 95 % (ref.[91]: 87 %), m.p. 133 °C (ref.[144]: 130–131 °C).

N–(2–methoxy–4–nitrophenyl) 3,5–dimethoxyanthranylic acid (**68**)



68

The synthesis of compound **68** was performed as described in reference[90] with some improvements. 0.50 g (2.50 mmol) of aniline **65**, 0.70 g (2.50 mmol) of reagent **67**, 0.10 g (1.5 mmol) of Cu and 0.050 g (0.62 mmol) of CuO were suspended in 20 mL DMF. Sodium acetate (0.21 g, 2.56 mmol) was used as base instead of K_2CO_3. The reaction was carried out at 120 °C for 1 h. The mixture was poured into 100 mL of water and 50 mL of 2 *N* NaOH and the mixture was filtered off. The filtrate was neutralised with 2 *N* HCl and the solid was collected by filtration. The remaining organic phase in the filtrate was extracted with ether (2 × 100 mL). Product **68** was purified by FC of the combined product fractions with toluene/EtOH (9/1) and further recrystallisation from MeOH: yellow needles (0.52 g, 1.50 mmol, 59 %), m.p. 218 °C.

^{1}H NMR (acetone–d_6): δ = 8.22 (s, 1 H, NH), 7.61 (dd, $^3J_{12,\,11}$ = 8.9 Hz, $^4J_{12,\,14}$ = 2.5 Hz, 1 H, 12–H), 7.57 (d, $^4J_{14,\,12}$ = 2.4 Hz, 1 H, 14–H), 7.03 (d, $^4J_{6,\,4}$ = 2.8 Hz, 1 H, 6–H), 6.81 (d, $^4J_{4,\,6}$ = 2.8 Hz, 1 H, 4–H), 6.21 (d, $^3J_{11,\,12}$ = 8.9 Hz, 1 H, 11–H), 3.92 (s, 3–H, 16–H), 3.76 (s, 3 H, 8–H), 3.72 (s, 3 H, 9–H).

^{13}C NMR (acetone–d_6): δ = 206.2 (s, C–7), 168.4 (s, C–15), 158.2 (s, C–5), 155.9 (s, C–3), 147.5 (s, C–13), 139.5 (s, C–10), 126.1 (s, C–2), 124.2 (s, C–1), 118.8 (d, C–11), 112.2 (d, C–12), 107.0 (d, C–14), 105.7 (d, C–6), 104.8 (d, C–4), 56.6 (q, C–8), 56.2 (q, C–16), 56.0 (q, C–9).

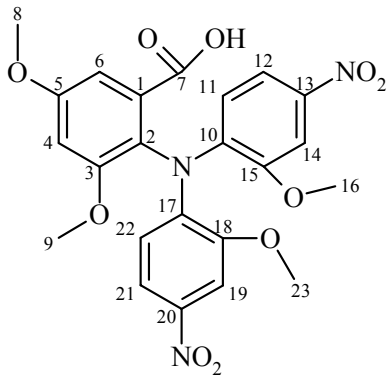
UV/vis (acetone): λ_{max} (lg ε) = 414 nm (4.21).

IR[1] (KBr): $\tilde{\nu}$ = 3380 cm^{-1} (m, val sec. N–H), 3096 (w, val. arom. C–H), 2991 (w), 2947 (w, val. aliph. C–H), 2925 (w), 2840 (w), 1674 (s, val. COOH), 1650 (m), 1610 (s, val. arom. C=C), 1590 (s), 1535 (s, val. asymm. NO_2), 1490 (vs, δ–arom. C=C), 1470 (s, δ–CH_3), 1460 (s), 1440 (s), 1384 (w), 1330 (vs, val. symm. NO_2), 1302 (s), 1272 (s, val. asymm. Ar–O–Me), 1257 (s), 1240 (s), 1218 (s), 1196 (s), 1184 (m); 1152 (m), 1096 (m), 1068 (m), 954 (w), 875 (w, 1,3,4–three subs. phenyl ring), 830 (w), 799 (w), 742 (w).

MS (EI): *m/z* (%): = 348(100) [M^+], 318 (10) [M–$HCHO^+$], 302 (6) [M–NO_2^+], 284 (8) [$K_{(302)}$–H_2O^+], 256 (5) [$K_{(284)}$–CO^+].

EA: $C_{16}H_{16}N_2O_7$ (348.33): calc. C 55.17 H 4.63 N 8.04
found: C 55.19 H 4.65 N 7.84.

N,N–bis–(2–methoxy–4–nitrophenyl) 3,5–dimethoxyanthranylic acid (**69**)



69

Derivative **69** was obtained as a by–product of the Ullmann synthesis of *N*-phenylanthranylic acid **68**. Purification was performed as described above for **68** and the amounts of **69** were collected and finally recrystallised from EtOH to give the pure substance. The raw yields varied between 4 and 25 %, depending of the conditions of the reaction. Compound **69** was isolated as dark yellow plates, m.p. 265 °C.

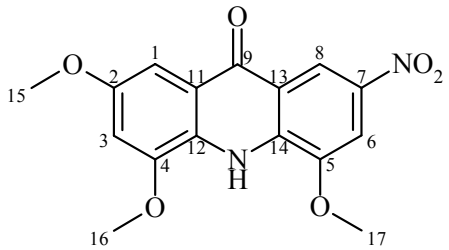
^{1}H NMR (acetone–d_6): δ = 7.60 (s, 2 H, 19–, 14–H), 7.59 (dd, $^3J_{21,22}$ = 6.1 Hz, $^4J_{21,19}$ = 1.9 Hz, 2 H, 21–, 12–H), 6.82 (d, $^4J_{6,4}$ = 2.8 Hz, 1 H, 6–H), 6.78 (d, $^3J_{11,12}$ = 9.0 Hz, 1 H, 11–H), 6.73 (d, $^4J_{4,6}$ = 2.8 Hz, 1 H, 4–H), 6.70 (d, d, $^3J_{22,21}$ = 9.5 Hz, 1 H, 22–H), 3.77 (s, 3 H, 8–H), 3.55 (s, 3 H, 9–H), 3.54 (s, 3 H, 16–H), 3.53 (s, 3 H, 23–H).

^{13}C NMR (acetone–d_6): δ = 167.3 (s, C–7), 160.4(s, C–5), 158.9 (s, C–3), 153.2 (d, C–18), 153.1 (d, C–15), 144.0 (s, C–17), 143.9 (s, C–10), 143.6 (s, C–20), 143.5 (s, C–13), 133.6 (s, C–2), 127.6 (s, C–6), 123.4 (d, C–21), 123.1 (d, C–12), 117.3 (d, C–22), 117.2 (d, C–11), 108.0 (d, C–19), 107.8 (d, C–14), 107.0 (d, C–6), 103.8 (d, C–4), 56.8 (q, C–16), 56.7 (q, C-23), 56.5 (q, C–9), 56.1 (q, C–8).

MS (EI): *m/z* (%): = 499 (100) [M^+], 469 (4) [M–$HCHO^+$], 453 (25) [M–NO_2^+].

EA: $C_{23}H_{21}N_3O_{10}$ (499.44): calc. C 55.31 H 4.24 N 8.41
found: C 55.37 H 4.26 N 8.35.

7–Nitro–2,4,5–trimethoxy (10–H) acridone (**70**)



70

Cyclisation of compound **68** was performed analogously to the procedure given by Brockmann *et al.*[90] 0.70 g (2.0 mmol) of **68** was dissolved in 30 g PPA (polyphosphoric acid) at 70 °C under nitrogen. The reaction was carried out at 100 °C for 1 h. After cooling to 60 °C the reaction mixture was poured into 200 mL cold water and neutralised with 30 %

NaOH (< 20 °C). The solid was filtered off and recrystallised from EtOH/DMF. Product **70** was obtained as deep–orange needles (0.40 g, 1.21 mmol, 61 %), m.p. 302–303 °C.

H NMR ($CDCl_3$): δ = 9.08 (s, 1 H, NH), 8.97 (d, $^4J_{8,6}$ = 2.2 Hz, 1 H, 8–H), 7.80 (d, $^4J_{6,8}$ = 2.2 Hz, 1 H, 6–H), 7.35 (d, $^4J_{1,3}$ = 2.4 Hz, 1 H, 1–H), 6.81 (d, $^4J_{3,1}$ = 2.4 Hz, 1 H, 3-H), 4.14 (s, 3 H, 17–H), 4.05 (s, 3 H, 15–H), 3.93 (s, 3 H, 16–H).

^{13}C NMR ($CDCl_3$): δ = 176.5 (s, C–9), 156.1 (s, C–5), 148.8 (s, C–2), 147.6 (s, C–4), 141.2 (s, C–7), 134.3 (s, C-14), 125.6 (s, C–12), 122.7 (s, C–11), 119.2(s, C–13), 116.4 (d, C–8), 104.8 (d, C–6), 104.7 (d, C–1), 96.7 (d, C–3), 56.7 (q, C–17), 56.3 (q, C–15), 55.9 (q, C–16).

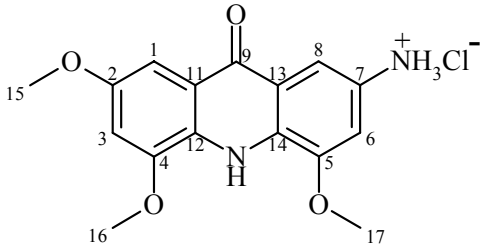
UV/vis ($CHCl_3$): λ_{max} (lg ε) = 246 nm (4.46), 310 (3.75), 378 (4.19), 428 (3.95).

IR[1] (KBr): $\tilde{\nu}$ = 3420 cm^{-1} (s, val. sec. N–H), 3112 (w), 3090 (w, val. arom. C–H), 3011 (w), 2997 (w), 2987 (w), 2945 (w, val. aliph. C–H), 2925 (w), 2873 (w), 2842 (w), 1639 (vs, val. C=O), 1602 (vs, val. arom. C=C), 1543 (vs, val. asymm. NO_2), 1514 (vs, δ–arom. C=C), 1498 (s), 1462 (s, δ–CH_2), 1454 (s), 1433 (m, δ–CH_3), 1371 (m), 1329 (vs, val. symm. NO_2), 1305 (vs), 1286 (s, val. asymm. Ar–O–C), 1252 (s), 1224 (m), 1213 (m), 1200 (s), 1187 (m), 1152 (s, val. C–O), 1089 (s), 1065 (s), 1004 (s), 935 (m), 898 (m, δ–isol. arom. H), 875 (m), 870 (m), 838 (m), 794 (m), 775 (w), 744 (m), 583 (m).

MS (EI): *m/z* (%): = 330 (100) [M^+], 300 (19) [M–$HCHO^+$], 285 (8) [M+H–NO_2^+], 269 (10) [$K_{(300)}$–CH_3O^+].

EA: $C_{16}H_{14}N_2O_6$ (330.31): calc. C 58.18 H 4.27 N 8.48
found: C 57.54 H 4.16 N 8.16.

7–Amino–2,4,5–trimethoxy (10–H) acridone, hydrochloride (**71**)



71

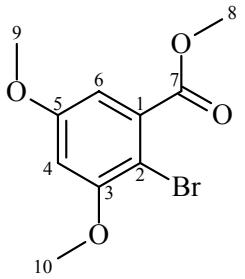
Substance **71** was synthesised according to Goldberg and Kelly.[103] 0.60 g (1.80 mmol) of **70** was suspended in 15 mL of EtOH and 15 mL of 10 *N* HCl and 1.25 g (5.53 mmol) of $SnCl_2$ dihydrate were added and the mixture was boiled for 1 h. The mixture was poured into 100 mL of ice. The solid was filtered off and stirred for 1 h in 2 *N* NaOH solution and was filtered again. The product **71** appeared as orange needles, which became brown on air. Converting amino–compound **71** to its hydrochloride it was possible to obtain satisfactory NMR spectra, but other analyses failed.

^{1}H NMR (DMSO–d_6): δ = 10.52 (br. s, 3 H, N$\underline{H}_3$Cl), 8.99 (s, 1 H, N$\underline{H}$), 7.73 (s, 1 H, 8–H), 7.26 (s, 1 H, 6–H), 7.14 (s, 1 H, 1–H), 7.01 (s, 1 H, 3–H), 4.06 (s, 3 H, 15–H), 4.03 (s, 3 H, 16–H), 3.86 (s, 1 H, 17-H).

^{13}C NMR (DMSO–d_6): δ = 168.5 (s, C–9), 156.2 (s, C–5), 147.8 (s, C–2), 143.6 (s, C–4), 141.0 (s, C–7), 135.3 (s, C-14), 127.6 (s, C–12), 125.7 (s, C–11), 120.2 (s, C–13), 110.0 (d, C–8), 106.8 (d, C–6), 104.4 (d, C–1), 56.7 (q, C–17), 56.6 (q, C–15), 56.4 (q, C–16).

MS (EI): *m/z* (%): = 300 (100) [M^+], 285 (34.7) [M–NH^+], 267 (7.0) [M+H–CH_3OH^+], 239 (5.8) [$K_{(285)}$–$HCHO^+$], 150 (14.0) [M–$C_6H_2(OCH_3)_2N^+$].

Methyl–2–bromo–3, 5–dimethoxybenzoate (**74**)



74

The bromination of methyl–3,5–dimethoxybenzoate **63a** was carried out according to Youngmin *et al.*[145] 7.0 g (35.27 mmol) of methyl–3,5–dimethoxybenzoate **63a** was dissolved in 50 mL of dry CH_3CN and 6.4 g (36.0 mmol) of NBS was added in one portion at 0 °C. The reaction was stirred for 16 h at room temperature. After completion of the reaction the solution was poured into 150 mL water and 100 mL of saturated Na_2SO_3 solution was added. The organic phase was extracted with ether (2 × 100 mL), dried with $MgSO_4$ and the solvent was removed by distillation. The residue was Kugelrohr–distilled under vacuum (155 °C,

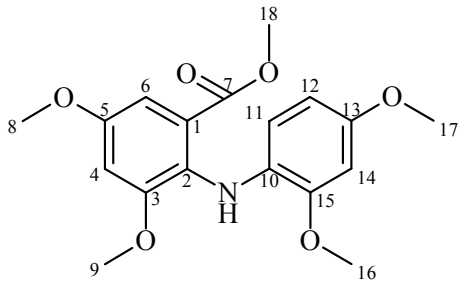
1.3 mm Hg). Product **74** was isolated as white plates (8.2 g, 29.8 mmol, 84 %, lit.[145]: 74 %), m.p. 58 °C (lit.[145]: 55–57 °C).

^{1}H NMR ($CDCl_3$, 200.13 MHz): δ = 6.79 (d, $^4J_{4,6}$ = 2.8 Hz, 1 H, 4–H), 6.58 (d, $^4J_{6,4}$ = 2.8 Hz, 1 H, 6–H), 3.93 (s, 3 H, 8–H), 3.89 (s, 3 H, 10–H), 3.82 (s, 3 H, 9–H).

^{13}C NMR ($CDCl_3$, 50.32 MHz): δ = 167.2 (s, C–7), 159.2 (s, C–5), 157.5 (s, C–3), 135.2 (s, C–1), 108.8 (d, C–6), 102.2 (d, C–4), 102.0 (s, C–2), 56.5 (q, C–8), 54.8 (q, C–10), 52.6 (q, C–9).

MS (EI): *m/z* (%): = 276 (100) [M^+, ^{81}Br], 274 (97) [M^+, ^{79}Br], 245 (61) [$M–CH_3O^+$].

Methyl–*N*–(2,4–dimethoxyphenyl) 3,5–dimethoxyanthranilate (**75**)



75

2.00 g (7.27 mmol) of **72**, 1.224 g (8.0 mmol) of 2,4–dimethoxyaniline **73**, 0.10 g (0.109 mmol) of $Pd(dba)_3$ and 0.089 g (0.160 mmol) of DPPF were suspended in 20 mL of dry toluene. 0.768 g (8.00 mmol) of NaO*t*-Bu was added and the mixture was kept at 100 °C for 12 h. After completion of the reaction the solvent was distilled off and the residue dissolved in ether and filtered off. The filtrate was poured into cold 2 *N* HCl, the organic phase was separated and the solvent was distilled. The residue was chromatographed with EtOAc/hexane (1:1). Compound **75** was obtained as yellow needles (0.54 g, 1.60 mmol, 21 %), m.p. 124 °C.

^{1}H NMR ($CDCl_3$): δ = 7.04 (d, $^4J_{6,4}$ = 2.8 Hz, 1 H, 6–H), 6.69 (d, $^4J_{4,6}$ = 2.8 Hz, 1 H, 4–H), 6.49 (d, $^4J_{14,12}$ = 2.5 Hz, 1 H, 14–H), 6.33 (d, $^3J_{11,12}$ = 8.5 Hz, 1 H, 11–H), 6.28 (dd, $^3J_{12,11}$ = 8.5 Hz, $^4J_{12,14}$ = 2.5 Hz, 1 H, 12–H), 3.90 (s, 3 H, 18–H), 3.83 (s, 3 H, 8–H), 3.81, (s, 3 H, 9–H), 3.75 (s, 3 H, 17–H), 3.74 (s, 3 H, 16–H).

^{13}C NMR ($CDCl_3$): δ= 167.9 (s, C–7), 154.7 (s, C–13), 154.0 (s, C–15), 153.9 (s, C–3), 149.7 (s, C–5), 129.1 (s, C–2), 128.0 (s, C–1), 121.3 (s, C–10), 115.1 (d, C–11), 104.6 (d, C-4, –14), 103.1 (d, C–6), 98.7 (d, C–12), 55.7 (q, C–18), 55.61 (q, C–8), 55.60 (q, C–9, –16), 52.1 (q, C–17).

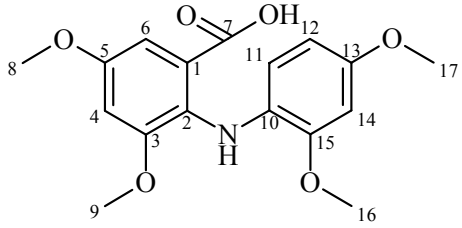
UV/vis ($CHCl_3$): λ_{max} (lg ε) = 246 nm (4.24), 310 (3.66 sh), 378 (3.76).

IR[2] (KBr): $\tilde{\nu}$ = 3335 cm^{-1} (m, val. sec. N–H), 3007 (w, val. arom. C–H), 2953 (w, val. aliph. C–H), 2936 (w), 2834 (w, val. aliph. COOC–H_3), 1689 (s, val. COOMe), 1604 (m, val. arom. C=C), 1513 (s), 1493 (s), 1454 (s, δ–CH_2), 1426 (s, δ–CH_3), 1349 (m), 1297 (m), 1261 (m, val. C-O–C), 1232 (s), 1153 (vs, val. C–O), 1063 (s), 1030 (s), 933 (s), 887 (m), 845 (w), 806 (m, 1,3,4–three subs. phenyl ring), 779 (w), 762 (m), 722 (m), 681 (w), 616 (m), 594 (m).

MS (EI): *m/z* (%): = 347 (100) [M^+], 332 (6) [M–CH_3^+], 314 (9) [$K_{(332)}$–H_2O^+], 301 (23) [M-$HCOOH^+$], 272 (10) [M–H–$CH_3COOCH_3^+$], 241 (10) [$K_{(272)}$–CH_3O^+].

EA: $C_{18}H_{21}NO_6$ (347.36) calc.: C 62.24 H 6.09 N 4.03
found: C 62.37 H 6.04 N 4.02.

N–(2,4–dimethoxyphenyl) 3,5–dimethoxyanthranilic acid (**76**)



76

The cleavage of the methyl group was performed as usual. 0.50 g (1.40 mmol) of compound **75** was saponified in 30 mL of EtOH and 3 mL of 2 *N* NaOH solution at reflux for 1 h. The solution was poured into ice to which 2 *N* HCl had been added (pH < 5). The crystals were filtered off and recrystallised from EtOH. **76** was produced as light–yellow plates (0.45 g, 1.35 mmol, 94 %), m.p. 194 °C.

^{1}H NMR ($DMSO–d_6$): δ= 13.30 (s, 1 H, COO<u>H</u>), 7.84 (s, 1 H, N<u>H</u>), 7.01 (d, $^4J_{6,4}$ = 2.8 Hz, 1 H, 6–H), 6.86 (d, $^4J_{4,6}$ = 2.8 Hz, 1 H, 4–H), 6.55 (d, $^4J_{14,12}$ = 2.6 Hz, 1 H, 14–H), 6.30 (dd,

$^3J_{12,\,11}$ = 8.6 Hz, $^4J_{12,\,14}$ = 2.6 Hz, 1 H, 12–H), 6.15 (d, $^4J_{11,\,12}$ = 8.6 Hz, 1 H, 11–H), 3.84 (s, 3 H, 8–H), 3.80 (s, 3 H, 9–H),3.71 (s, 3 H, 17–H),3.69 (s, 3 H, 16–H).

^{13}C NMR (DMSO–d_6): δ = 168.7 (s, C–7), 154.5 (s, C–13), 153.9 (s, C–15), 153.1 (s, C–3), 148.9 (s, C–5), 127.8 (s, C–2), 127.7 (s, C–1), 122.4 (s, C–10), 114.4 (d, C–11), 105.1 (d, C-6), 104.4 (d, C–12), 103.6 (d, C–4), 98.8 (d, C–14), 55.6 (q, C–8), 55.4 (q, C–9, –16), 55.3 (q, C–17).

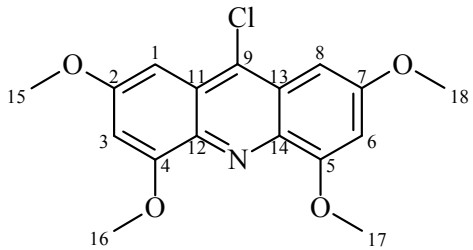
UV/vis (DMSO): λ_{max} (lg ε) = 262 nm (4.02), 310 (3.78), 346 (3.67).

IR[2] (KBr): $\tilde{\nu}$ = 3359 cm^{-1} (w, val. sec. N–H), 3006 (w, val. arom. C–H), 2944 (w, val. aliph. C–H, CH_3), 2906 (w), 2834 (w, val. aliph. C–H, CH_2), 2555 (w, val. COOH, dimer structures), 1658 (s, val. C=OOH), 1598 (s, val. arom. C=C), 1514 (s, δ–arom. C=C), 1494 (s), 1457 (vs, δ– CH_3), 1436 (s), 1411 (s), 1345 (m), 1325 (m), 1295 (m), 1267 (s, val. C–O–C), 1235 (vs), 1206 (vs), 1184 (s), 1155 (vs, val C–O), 1111 (s), 1061 (s), 1052 (m), 1052 (m), 1031 (vs), 936 (m), 911 (m), 852 (m), 838 (s, δ–isol. arom. H), 815 (m), 793 (m), 780 (m), 734 (m), 719 (w), 687 (w).

MS (EI): *m/z* (%): = 333 (7) [M^+], 331 (55) [M–H_2^+], 317 (82) [M–O^+], 300 (> 0.1) [M-CHO^+], 179 (89) [M–$C_6H_3(OCH_3)_2$–NH_3^+], 165 (100) [M–CO_2–4·CH_3O^+].

EA: $C_{17}H_{19}NO_6$ (333.37): calc. C 61.25 H 5.75 N 4.20
found: C 61.19 H 5.67 N 4.24.

9–Chloro–2,4,5,7–tetramethoxyacridine (**80**)



80

Acridine **80** was synthesised analogously to Lehmstedt and Schrader.[106] 0.40 g (1.20 mmol) of **76** was dissolved in 20 mL of $POCl_3$ and the mixture was refluxed for 90 min. The $POCl_3$ was distilled off, the rest was cooled to room temperature and 60 mL of $CHCl_3$ was added.

The suspension was poured into excess of ice–ammonia (150 mL) and the mixture was stirred for 10 min. The organic phase was separated, washed with plenty of water, dried with $MgSO_4$ and the solvent was removed *in vacuo*. Recrystallisation from DMF/water afforded product **80** as orange needles (0.238 g, 0.714 mmol, 60 %), m.p. 224 °C.

^{1}H NMR (DMSO–d_6): δ = 7.02 (d, $^4J_{1,3}$ = 2.4 Hz, 2 H, 1–, 8–H), 6.81 (d, $^4J_{3,1}$ = 2.6 Hz, 2 H, 3–, 6–H), 4.01 (s, 6 H, 15–, 18–H), 3.98 (s, 6 H, 16–, 17–H).

^{13}C NMR (DMSO–d_6): δ = 159.2 (s, C–2, –7), 156.9 (s, C–4, –5), 135.6 (s, C–12, –14), 133.6 (s, C–11, –13), 125.9 (s, C–9), 101.3 (d, C–1, –8), 91.5 (d, C–3, –6), 56.0 (q, C–15, -18), 55.6 (q, C–16, –17).

UV/vis ($CHCl_3$): λ_{max} (lg ε) = 236 nm (3.98), 276 (4.02), 308 (3.82), 374 (3.91), 394 (3.72), 416 (3.59).

IR[2] (KBr): $\tilde{\nu}$ = 3113 cm^{-1} (w, val. arom. C–H), 3034 (w), 3008 (w), 2963 (w, val. aliph. C–H, CH_3), 2930 (w), 2831 (w), 1613 (vs, val. arom. C=C), 1563 (s), 1532 (m), 1473 (m), 1444 (m), 1411 (vs, δ–CH_3), 1332 (s), 1255 (s), 1234 (m), 1202 (vs, val. C–O), 1143 (s, val. C–O–C), 1112 (m, val. arom. C–Cl), 1042 (m), 1000 (m), 930)m), 856 (w), 818 (vs, δ–isol. arom. H-atoms), 776 (s), 675 (m).

MS (EI): *m/z* (%): = 333 (100) [M^+], 315 (20) [M–H_2O^+], 304 (62) [M–CHO^+], 289 (64) [M–CO_2^+], 254 (22) [$K_{(289)}$–$^{35}Cl^+$].

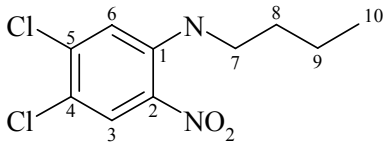
EA: $C_{17}H_{16}ClNO_4$ (333.75): calc. C 61.18 H 4.83 N 4.20
found: C 61.04 H 4.86 N 4.07.

5.5. Trimethine dyes

5.5.1. Halogen–trimethines

5.5.1.1. Bis-*n*-butyl–tetrachloro–trimethine

N–Butyl–4,5–dichloro–2–nitroaniline (**90**)



90

Compound **90** was obtained as described in the literature[40a] using ethyl diisopropylamine (EDPA) as a base. 50.9 g (210.0 mmol) of 2,4,5–trichloronitrobenzene **89**, 15.4 g (210.6 mmol) of *n*–butylamine and 27.2 g (35.8 mL, 211 mmol) of EDPA were dissolved in 125 mL of *i*–PrOH. The solution was kept under reflux for 8 h and then cooled to room temperature. After 24 h in the refrigerator the orange needles were filtered off and the filtrate was concetrated to 1/3 of its volume. The remaining solution was placed in the refrigerator for another 24 h. This procedure was repeated and the product obtained was recrystallised again from *i*–PrOH. The crystals were washed with cold MeOH and dried *in vacuo* (47.5 g, 180.6 mmol, 86 %, lit.[40a]: 48 %), m.p. 66–67°C (lit.[40a]: 62–63°C).

^{1}H NMR (DMSO–d_6): δ = 8.25 (s, 1 H, 6–H), 7.94 (br. s, 1 H, NH), 6.94 (s, 1 H, 3–H), 3.26 (q, $^3J_{7,\,NH}$ = 3.5 Hz, $^3J_{7,\,8}$ = 7.1 Hz, 2 H, 7–H), 1.72 (p, $^3J_{8,\,7}$ = 7.1 Hz, $^3J_{8,\,9}$ = 3.5 Hz, 2 H, 8-H), 1.47 (sx, $^3J_{9,\,8}$ = 3.5 Hz, $^3J_{9,\,10}$ = 7.3 Hz, 2 H, 9–H), 0.98 (t, $^3J_{10,\,9}$ = 7.3 Hz, 3 H, 10–H).

^{13}C NMR (DMSO–d_6): δ = 144.1 (s, C–1), 141.1 (s, C–5), 130.3 (s, C–2), 127.7 (d, C–3), 118.4 (s, C–4), 115.0 (d, C–6), 43.0 (t, C–7), 30.8 (t, C–9), 20.1 (t, C–8), 13.7 (q, C–10).

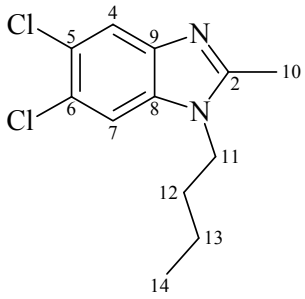
UV/vis (CH_3CN): λ_{max} (lg ε) =202 nm (4.25), 248 (4.44), 438 (3.81).

IR[1] (KBr): $\tilde{\nu}$ = 3381 cm^{-1} (s, val. sec. arom. N–H), 3303 (m), 3109 (m, val. arom. C–H), 3085 (m), 3017 (m), 2966 (s, val. aliph. C–H_3), 2934 (s, val. aliph C–H), 2864 (s), 2868 (s),

1622 (vs, val. arom. C=C), 1555 (vs, val. asymm. NO_2), 1512 (s, δ–arom C=C), 1480 (vs), 1466 (vs, δ-CH_2), 1420 (s, δ–CH_3), 1405 (vs), 1386 (s, val. sym. NO_2), 1337 (s), 1287 (vs), 1264 (vs), 1252 (vs), 1216 (vs), 1141 (vs), 1124 (s), 1091 (s), 1067 (s, val. arom. C–Cl), 1061 (s, arom. C–Cl), 956 (vs), 900 (s), 890 (vs), 842 (s, δ–isol. arom–H), 759 (s), 732 (s), 677 (vs), 541 (s), 530 (s).

MS (EI): *m/z* (%): = 264 (15) [M^+], 219 (100) [M–$C_3H_7^+$].

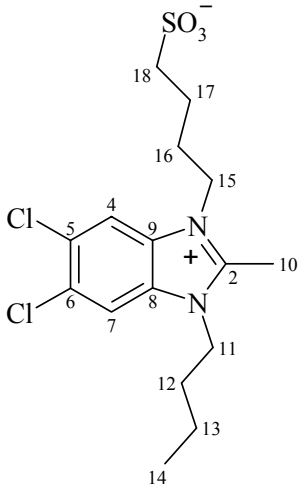
1–Butyl–5,6–dichloro–2–methylbenzimidazole (**91**)



91

The synthesis of compound **91** is described in reference.[40a] 26.32 g (100.0 mmol) of the intermediate **90** and 30.08 g (460.0 mmol) Zn–powder were mixed in 100 mL of 1,2-dichloroethane. The mixture was heated up to 100 °C and 150 mL of acetic acid was carefully added dropwise under vigorous stirring for 1 h. Acetic anhydride (75.0 mL) was added and the mixture was kept under reflux for 16 h. After completing the reaction the mixture was cooled to room temperature, filtered, poured into 200 mL of ice–water and neutralised with 200 mL 5 *N* NaOH solution. The organic phase was extracted (4 × 100 mL) with 1,2–dichloroethane, washed with water (200 mL) and dried with $MgSO_4$. The solvent was distilled off and the crude product recrystallised from EtOAc/*n*–hexane. The solid was filtered off and dried *in vacuo* (21.53 g, 83.7 mmol, 83 %), m. p. 114°C (lit.[40a]: 88 %, m. p. 106–108) and used without further purification.

1–Butyl–5,6–dichloro–2–methyl–3–(4–sulphobutyl) benzimidazoliumbetaine (**101**)



101

Preparation of compound **101** was carried out as given in literature[40a], and also described by Pawlik *et al.*[123, 146] 21.42 g (83.3 mmol) of benzimidazole **91** and 13.10 g (96.2 mmol) 1,4-butanesultone **97b** were dissolved in 25 mL of 1,2–dichlorobenzene. The solution was heated at 130 °C for 3 h and during that time betaine **101** fell out. The temperature was increased to 140 °C for 1 h and the mixture slowly cooled to room temperature. The solid was filtered off and recrystallised from EtOH/DMF. **101** appeared as white plates (yield 19.66 g, 50.00 mmol, 60 %), m.p. 310–312 °C.

^{1}H NMR (D_2O): δ = 8.06 (s, 1 H, 4–H), 8.03 (s, 1 H, 7–H), 4.8 (s, 3 H, 10–H), 4.49 (t, $^3J_{11,\,12}$ = 7.0 Hz, 2 H, 11–H), 4.44 (t, $^3J_{15,\,16}$ = 7.3 Hz, 2 H, 15–H). 4.97 (t, $^3J_{18,\,17}$ = 7.6 Hz, 2 H, 18–H), 4.07 (t, $^3J_{12,\,13}$ = 7.4 Hz, 2 H, 12–H), 1.88 (m, 4 H, 16–, 17–H), 1.41 (sx, $^3J_{13,\,12}$ = 7.4 Hz, $^3J_{13,\,14}$ = 7.4 Hz, 2 H, 13–H), 0.96 (t, $^3J_{14,\,13}$ = 7.4 Hz, 3 H, 14–H).

^{13}C NMR (D_2O): δ = 155.3 (s, C–2), 134.9 (s, C–8), 134.8 (s, C–9), 134.6 (s, C–5, –6), 116.9 (d, C–4), 116.8 (d, C–7), 54.7 (t, C–18), 48.5 (t, C–15), 48.0 (t, C–11), 34.9 (t, C–13), 29.6 (t, C–16), 23.9 (t, C–17), 21.9 (t, C–12), 13.7 (q, C–14).

UV/vis (DMSO): λ_{max} (lg ε) = 264 nm (4.05), 288 (4.16), 296 (14.12).

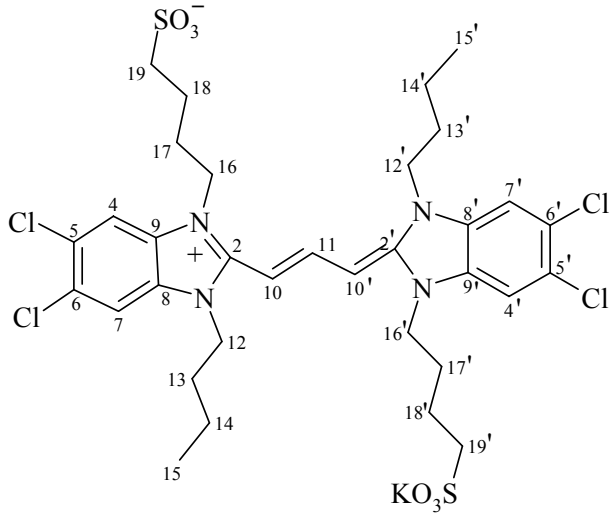
IR[2] (KBr): $\tilde{\nu}$ = 3099 cm^{-1} (w, val. arom. C–H), 3007 (w), 2960 (w, aliph. C–H, CH_3), 2933 (w, aliph. C–H, CH_2), 2876 (w), 1522 (w), 1470 (m, δ–CH_2), 1419 (w, δ–CH_3), 1378 (w), 1220 (w), 1188 (vs, val. asymm. SO_3^-), 1108 (w), 1036 (s, val. symm. SO_3^-), 601 (w).

MS (FAB+): *m/z* (%): = 393 (100) [M^+], 311 (14) [$M–H_2SO_3^+$].

EA: $C_{16}H_{22}Cl_2N_2O_3S$ (393.33): calc. C 48.86 H 5.64 N 7.12

found: C 48.55 H 5.65 N 7.02.

1–Butyl–2–{3–[1–butyl–5, 6–dichloro–1,3–dihydro–3–(4–sulphobutyl) 2H–benzimidazol–2–ylidene]–1–propenyl} 5,6–dichloro–3–(4–sulphobutyl)–benzimidazole, inner salt, as potassium salt (**104**)



104

The coupling of compound **101** with iodoform is described in reference.[40a] 4.00 g (5.09 mmol) of **101** and 1.05 g (4.66 mmol) of iodoform were mixed in 15 mL of dry MeOH and stirred vigorously under nitrogen. 1.23 g (11.0 mmol) of KO*t*-Bu was added in one portion and immediately a dark red colour appeared. After 30 min the temperature was increased to 50 °C for 5 min and then cooled to room temperature. The solid was filtered off, washed with small amounts of water and cold acetone and dried over $CaCl_2$. Double hot–extraction with EtOH yielded trimethine **104** as dark red crystals with strong yellow–green metallic lustre (1.00 g, 1.20 mmol, 48 %), m. p. (decomp.) 273 °C. The substance is known, but only the absorption maxima (water - 584 nm) has been given.[146]

^{1}H NMR (DMSO–d_6, 100°C): δ = 7.94 (s, 2 H, 4–, 4'–H), 7.83 (s, 2 H, 7–, 7'–H), 7.81 (t, $^3J_{11,\,10}$ = 13.4 Hz, 1 H, 11–H), 5.85 (d, $^3J_{10,\,11}$ = 13.3 Hz, 2 H, 10–, 10'–H), 4.29 (t, $^3J_{12,\,13}$ = 7.2 Hz, 8 H, 12–, 16–, 12'–, 16'–H), 4.55 (t, $^3J_{19,\,18}$ = 7.1 Hz, 4 H, 19–, 19'–H), 1.95 (p, $^3J_{13,\,12}$ = 7.2 Hz, $^3J_{13,\,14}$ = 7.7 Hz, 4 H, 13–, 13'–H), 1.77 (m, 8 H, 18–, 17–, 18'–, 17'–H),

1.35 (sx, $^3J_{14,\,13}$ = 7.4 Hz, $^3J_{14,\,15}$ = 7.3 Hz, 4 H, 14–, 14'–H), 0.91 (t, $^3J_{15,\,14}$ = 7.3 Hz, 6 H, 15–, 15'–H).

^{13}C NMR (DMSO–d_6, 100 °C): δ = 149.4 (s, C–2, –2'), 141.8 (d, C–11), 131.8 (s, C–8, –8', -9, –9'), 125.8 (s, C–6, –6'), 125.7 (s, C–5, –5'), 111.3 (d, C–4, –4'), 111.0 (d, C–7, –7'), 84.9 (d, C–10, –10'), 50.2 (t, C–19, -19'), 44.5 (t, C–16, –16'), 44.4 (t, C–12, –12'), 29.2 (t, C–14, -14'), 26.2 (t, C–17, –17'), 21.8 (t, C–18, –18'), 18.7 (t, C–13, –13'), 14.9 (q, C–15, –15').

UV/vis (DMF): λ_{max} (lg ε) = 278 nm (3.92), 526 (4.91).

UV/vis (DMF/pH 11, NaCl = 0.3 M): λ_{max} (lg ε) = 310 nm (3.54), 522 (5.06), 586 (4.60).

UV/vis (DMF/pH11, NaCl = 0.6 M): λ_{max} (lg ε) = 310 nm (3.67), 522 (4.88), 588 (4.86).

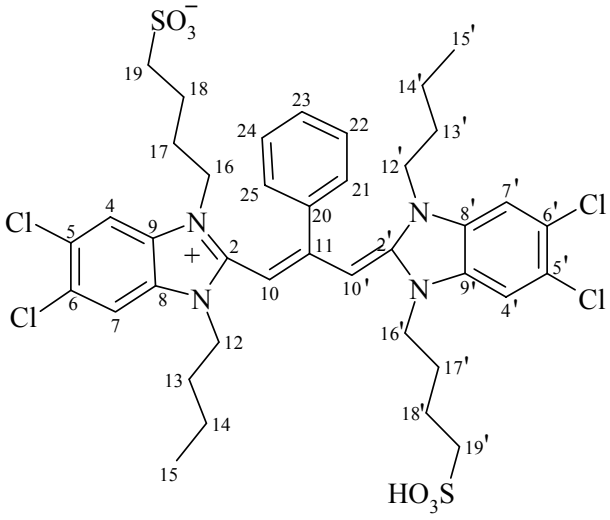
UV/vis (EtOH): λ_{max} (lg ε) = 210 nm (4.75), 276 (3.94), 492 (4.80 sh), 522 (5.07).

IR[2] (KBr): $\tilde{\nu}$ = 3104 cm^{-1} (w, val. arom. C–H), 3040 (w), 2959 (w, aliph. C–H, CH_3), 2932 (w, val. aliph. C–H, CH_2), 2871 (w), 1676 (m, C–N), 1551 (vs, val. arom. C=C), 1478 (s), 1428 (vs, δ–CH_3), 1311 (s), 1246 (m), 1168 (m), 1148 (m), 1108 (m, val. arom. C–Cl), 1039 (m), 913 (w), 860 (w, δ–isol. arom–H), 791 (w), 607 (w), 579 (w).

MS (ESI): *m/z* (%): = 855 (25) [(Na^+M^-)K^+], 839 (36) [(Na^+M^-)Na^+]; [(M–H) K^+, 4 ^{37}Cl], 717 (25) [M–SO_3^+], 661 (44) [M-$C_4H_8SO_3^+$].

EA: $C_{33}H_{42}Cl_4KN_4O_6S_2 \cdot 1\ H_2O$ (853.79): calc. C 46.48 H 5.19 N 6.57
found: C 46.49 H 5.14 N 6.64.

1–Butyl–2–{3–[1–butyl–5,6–dichloro–1,3–dihydro–3–(4–sulphobutyl) 2H–benzimidazol–2–ylidene]–2–phenylpropen–1–yl} 5,6–dichloro–3–(4–sulphobutyl)–benzimidazole, inner salt (**107**)



107

1.18 g (3.00 mmol) of betaine **101** and 0.32 g (1.64 mmol) of α,α,α–trichlorotoluene **100** were mixed in 15 mL of dry MeOH. 0.784 g (7.00 mmol) KO*t*-Bu was added in one portion under nitrogen and the mixture vigorously stirred. The mixture was kept under reflux for 5 h and then cooled to room temperature. The solid was filtered off and chromatographed with toluene/MeOH (1/1) on Al_2O_3 and subsequently on RP–SiO_2 with MeOH/water (3/7). The dye **107** was isolated as dark red crystals (0.11 g, 0.13 mmol, 8 %), m.p. (decomp.) 235 °C.

^{1}H NMR (DMSO–d_6): δ = 8.02 (s, 2 H, 4–, 4'–H), 7.95 (s, 2 H, 7–, 7'–H), 7.49 (m, 5 H, 21-, 22–, 23–, 24–, 25–H), 5.24 (s, 2 H, 10–, 10'–H), 4.09 (br. s, 4 H, 16–, 16'–H), 3.98 (br. s, 4 H, 12–, 12'–H), 4.43 (t, $^3J_{19,\,18}$ = 7.3 Hz, 4 H, 19–, 19'–H), 1.51 (m, 4 H, 13–, 13'–H), 1.77 (m, 8 H, 18–, 17–, 18'–, 17'–H), 1.16 (sx, $^3J_{14,\,13}$ = 7.6 Hz, $^3J_{14,\,15}$ = 7.4 Hz, 4 H, 14–, 14'–H), 0.81 (t, $^3J_{15,\,14}$ = 7.5 Hz, 6 H, 15–, 15'–H).

^{13}C NMR (DMSO–d_6): δ = 154.5 (s, C–2, –2'), 131.94 (s, C–8, –8'), 131.87 (s, C–9, –9'), 130.1 (s, C–11), 129.8 (d, C–23), 128.8 (d, C–21, –25'), 128.4 (d, C–22, –24'), 126.44 (s, C-20), 126.37 (s, C–6, –6'), 126.27 (s, C–5, –5'), 114.43 (d, C–4, –4'), 114.38 (d, C–7, –7'), 88.0 (d, C–10, –10'), 50.3 (t, C–19, –19'), 44.8 (t, C–16, –16'), 44.5 (t, C–12, –12'), 29.2 (t, C–14, –14'), 26.3 (t, C–17, 17'), 21.8 (t, C–18, –18'), 18.9 (t, C–13, –13'), 13.2 (q, C–15, -15').

UV/vis (CH_2Cl_2): λ_{max} (lg ε) = 230 nm (4.50), 274 (4.26), 334 (4.22), 538 (4.79).

UV/vis (EtOH): λ_{max} (lg ε) = 210 nm (4.80), 270 (4.19), 302 (4.07), 332 (4.21), 536 (4.73).

UV/vis (DMSO): λ_{max} (lg ε) = 270 nm (4.20), 300 (4.08), 336 (4.25), 544 (4.67).

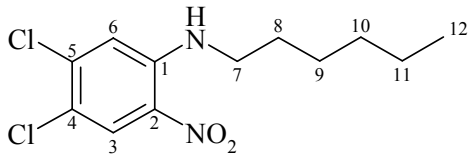
IR[2] (KBr): $\tilde{\nu}$ = 3075 cm^{-1} (w, arom. C–H), 3021 (w), 2958 (w, aliph. C–H, CH_3), 2929 (w), 2868 (w, aliph. C–H, CH_2), 1645 (w), 1498 (m), 1462 (s, δ– CH_2), 1423 (m), 1374(w), 1175 (vs, val. asymm. SO_3^-), 1111 (m, val. arom. C–Cl), 1033 (vs, val. symm. SO_3^-), 894 (w), 844 (w, δ–isol. arom–H), 755 (w), 599 (m).

MS (ESI): *m/z* (%): = 971 (100) [$(Na^+M^-)Na^+$], 911 (44) [KM^+], 895 (61) [NaM^+], 873 (34) [$M+H^+$], 809 (64) [$M+H–SO_2^+$].

EA: $C_{39}H_{47}Cl_4N_4O_6S_2$ (873.77): calc. C 53.61 H 5.42 N 6.41
found: C 54.13 H 5.71 N 6.37.

5.5.1.2. Bis-*n*-hexyl–tetrachloro–trimethine

4,5–Dichloro–*N*–hexyl–2–nitroaniline (**92**)



92

Aniline **92** was synthesised as described for compound **90**. 11.50 g (50.0 mmol) of 2,4,5–trichloronitrobenzene **89**, 7.76 g (60.10 mmol) of EDPA and 6.07 g (60.0 mmol) of hexylamine were dissolved in 40 mL of *i*–PrOH. The solution was refluxed for 16 h, cooled and diluted with 50 mL of EtOH. After staying overnight in the refrigerator orange crystals were collected by filtration. The filtrate was concentrated to ½ of his volume and placed in the refrigerator again. After filtration the product **92** was collected as orange needles (11.2 g, 38.46 mmol, 77 %), m.p. 43 °C.

^{1}H NMR ($CDCl_3$): δ = 8.26 (s, 1–H, 3–H), 7.95 (br. s, 1–H, N<u>H</u>), 6.94 (s, 1 H, 6–H), 3.26 (q, $^3J_{7,\,NH}$ = 5.4 Hz, $^3J_{7,\,8}$ = 7.1 Hz, 2 H, 7–H), 1.74 (p, $^3J_{8,\,7}$ = 7.1 Hz, $^3J_{8,\,9}$ = 7.4 Hz, 2 H, 8–H), 1.46 (m, 2 H, 9-H), 1.35 (m, 4 H, 10–, 11–H), 0.91 (t, $^3J_{12,\,11}$ = 5.5 Hz, 3 H, 12–H).

^{13}C NMR ($CDCl_3$): δ = 144.1 (s, C–1), 141.1 (s, C–2), 130.3 (s, C–5), 127.7 (d, C–3), 118.4 (s, C–4), 115.0 (d, C–6), 43.3 (t, C–7), 31.3 (t, C–10), 28.7 (t, C–9), 26.6 (t, C–8), 24.5 (t, C-11), 13.9 (q, C-12).

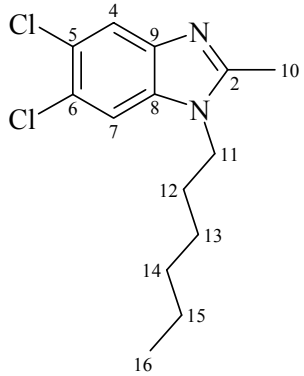
UV/vis ($CHCl_3$): λ_{max} (lg ε) = 206 nm (4.03), 246 (4.43), 290 (3.73), 430 (3.78).

IR[1] (KBr): $\tilde{\nu}$ = 3442 cm^{-1} (m, sec. N–H), 3384 (s), 3107(m, arom C–H), 3083 (m), 3020 (w), 2966 (s, val. aliph. C–H, CH_3), 2957 (s), 2932 (vs, aliph. C–H, CH_2), 2908 (s), 2872 (s), 2860 (s), 1618 (vs, arom. C=C), 1558 (vs, val. asymm. NO_2), 1514 (s), 1484 (vs), 1471 (vs, δ aliph CH_2), 1422 (m), 1408 (s), 1386 (s, val. symm. NO_2), 1337 (s), 1274 (vs), 1258 (vs), 1236 (vs), 1220 (vs), 1141 (s), 1074 (s, val. arom. C–Cl), 952 (s), 896 (m), 846 (m, δ–isol. arom. H), 761 (s), 736 (m), 728 (m), 678 (s), 521 (s).

MS (EI): *m/z* (%): = 292 (11) [M^+], 219 (100) [$M–C_5H_{11}^+$].

EA: $C_{12}H_{16}Cl_2N_2O_2$ (291.18): calc. C 49.50 H 5.54 N 9.62 Cl 24.35
found: C 49.66 H 5.69 N 9.55 Cl 24.48.

5,6–Dichloro–1–hexyl–2–methylbenzimidazole (**93**)

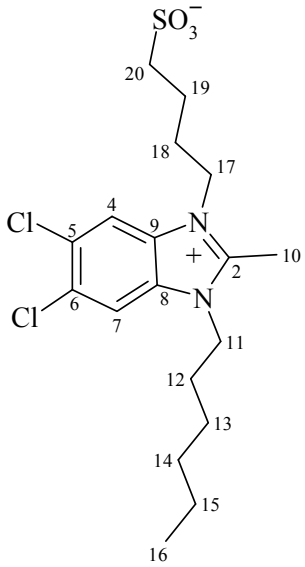


93

Reductive cyclisation of aniline **92** was carried out as described above for **91**. In 50 mL 1,2–dichloroethane were added 14.5 g (44.93 mmol) of intermediate **92** and 15.0 g (236.6 mmol) of Zn–powder. 75 mL of acetic acid (first) and 40 mL of acetic anhydride were added

dropwise to the mixture while vigorously stirring and refluxing for 2 h. After 24 h and cooling, neutralisation, extraction (2 × 100 mL) with 1,2–dichloroethane and further distillation of the solvents a residue was obtained, which was recrystallised twice from hexane. Product **93** appeared as white needles (7.10 g, 24.90 mmol, 58 %), m.p. 119 °C. (lit.[147] 120 °C).

5,6–Dichloro–1–hexyl–2–methyl–3–(4–sulphobutyl) benzimidazoliumbetaine (**102**)



102

Betaine **102** was synthesised by the quaternisation procedure given for compound **101**. 7.60 g (26.60 mmol) of benzimidazole **93** and 5.45 g (40.0 mmol) of 1,4–butanesultone **97b** were mixed in 1,2–dichlorobenzene and the reaction mixture was heated at 130 °C for 9 h under nitrogen. After 5 h the solid was filtered off and additionally 4.00 g (14.7 mmol) 1,4-butanesultone **97b** was added. At the end of reaction, the mixture was cooled, diluted with 150 mL of hexane and filtered. The resulting solid was boiled in 100 mL of EtOH for 30 min and filtered while hot. The product **102** was obtained as colourless prisms, which became light pink colour on standing (8.10 g, 19.24 mmol, 74 %), m.p. 301 °C.

^{1}H NMR (DMSO–d_6): δ = 8.54 (s, 1 H, 4–H), 8.41 (s, 1 H, 7–H), 4.51 (t, $^3J_{17,\,18}$ = 7.7 Hz, 2 H, 17–H), 4.44 (t, $^3J_{11,\,12}$ = 7.7 Hz, 2 H, 11–H), 4.95 (s, 3 H, 10–H), 1.99 (p, $^3J_{12,\,11}$ = 7.4 Hz, $^3J_{12,\,13}$ = 7.7 Hz, 2 H, 12–H), 1.81 (t, $^3J_{20,\,19}$ = 7.9 Hz, 2 H, 20–H), 1.75 (m, 2 H, 19–H), 1.41 (m, 2 H, 18–H), 1.33 (m, 6 H, 13–, 14–, 15–H), 0.89 (t, $^3J_{16,\,15}$ = 6.9 Hz, 3 H, 16–H).

^{13}C NMR (DMSO–d_6): δ = 154.2 (s, C–8), 130.2 (s, C–2), 130.0 (s, C–9), 128.9 (s, C–6), 128.8 (s, C–5), 115.2 (d, C–4), 114.7 (d, C–7), 50.3 (t, C–20), 45.7 (t, C–17), 45.6 (t, C–11), 30.6 (t, C–19), 28.2 (t, C-18), 27.1 (t, C–12), 25.4 (t, C–13), 24.0 (t, C–14, –15), 13.9 (q, C-10), 10.7 (q, C–16).

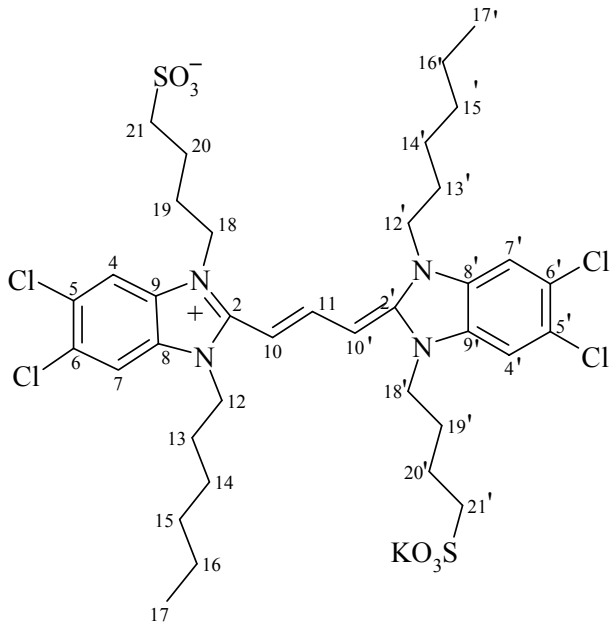
UV/vis (DMSO): λ_{max} (lg ε) = 264 nm (4.25), 288 (4.32), 296 (4.26 sh).

IR[2] (KBr): $\tilde{\nu}$ = 3000 cm^{-1} (w, val. arom C–H), 2959 (w, val. aliph. C–H, CH_3), 2930 (w, val. aliph. C-H, CH_2), 2872 (w), 1523 (w), 1467 (m, δ– CH_2), 1417 (w, δ– CH_3), 1377 (w), 1299 (w), 1220 (w), 1182 (vs, val. asymm. SO_3^-), 1108 (w), 1034 (s, val. symm. SO_3^-), 935 (w), 882 (w), 844 (w, δ–isol. arom–H), 778 (m), 751 (w), 645 (w), 598 (s), 537 (m).

MS (EI): *m/z* (%): = 422 (0.3) [M^+], 284 (83) [M-$C_4H_8SO_3^+$], 213 (100) [$K_{(284)}$–$C_5H_{11}^+$].

EA: $C_{18}H_{26}Cl_2N_2O_3S$ (421.36): calc. C 51.31 H 6.22 N 6.65 Cl 16.83
found: C 51.46 H 6.31 N 6.56 Cl 16.58.

5,6–Dichloro–2–{3–[5,6–dichloro–1,3–dihydro–1–hexyl–3–(4–sulphobutyl) 2H–benzimidazol–2–ylidene]–1–propenyl} 1–hexyl–3–(4–sulphobutyl)–benzimidazole, inner salt, potassium salt (**105**)



105

The trimethine **105** was synthesised by the method given for dye **104**. 4.21 g (10.0 mmol) of betaine **102** and 4.40 g (6.00 mmol) iodoform were suspended in 50 mL of MeOH. 4.80 g (25.00 mmol) of KO*t*-Bu was added in one portion and the mixture was stirred 1 h at ambient temperature and additionally for 1 h at 60 °C. The solid was filtered off and hot–extracted twice with MeOH (40 mL): **105** was isolated as dark red crystals with a strong green lustre (0.67 g, 0.75 mmol, 15 %), m.p. (decomp.) 230–233 °C.

^{1}H NMR (DMSO–d_6, 100 °C): δ = 7.95 (s, 2 H, 4–, 4'–H), 7.85 (s, 2 H, 7–, 7'–H), 7.82 (t, $^3J_{11,\,10}$ = 13.4 Hz, 1 H, 11–H), 5.86 (d, $^3J_{10,\,11}$ = 13.4 Hz, 2 H, 10–, 10'–H), 4.30 (dd, $^3J_{12,\,13}$ = 7.4 Hz, $^3J_{18,\,19}$ = 8.0 Hz, 8 H, 18–, 18'–, 12–, 12'–H), 2.55 (t, $^3J_{21,\,20}$ = 7.5 Hz, 4 H, 21–, 21'–H), 1.95 (p, $^3J_{13,\,12}$ = 7.4 Hz, $^3J_{13,\,14}$ = 7.4 Hz, 4 H, 13–, 13'–H), 1.80 (m, 8 H, 19–, 19'–, 20–, 20'–H), 1.33 (m, 12 H, 14–, 14'–, 15–, 15'–, 16–, 16'–H), 0.83 (t, $^3J_{17,\,16}$ = 8 Hz, 6 H, 17–, 17'–H).

^{13}C NMR (DMSO–d_6, 100 °C): δ = 149.4 (s, C–2, –2'), 141.7 (d, C–11), 131.79 (s, C–2, –2'), 131.76 (s, C–9, –9'), 125.7 (s, C–6, –6'), 125.6 (s, C–5, –5'), 111.3 (d, C–4, –4'), 110.9 (d, C-7, –7'), 84.8 (d, C–10, –10'), 50.1 (t, C–21, –21'), 44.5 (t, C–12, –18, –12', –18'), 30.2 (t, C-15, –15'), 26.9 (t, C–20, –20'), 26.2 (t, C–13, –13'), 24.9 (t, C–14, –14'), 21.8 (t, C–19, -19'), 21.2 (t, C–16, –16'), 12.9 (q, C–17, –17').

UV/vis (DMSO): λ_{max} (lg ε) = 280 nm (4.05), 504 (4.92 sh), 528 (5.22).

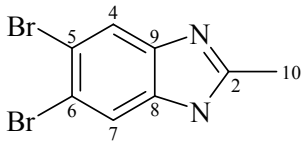
IR[2] (KBr): $\tilde{\nu}$ = 3405 cm^{-1} (w), 3021 (w, val. arom. C–H), 2957 (w, val. aliph. C–H, CH_3), 2925 (w, val. aliph. C–H, CH_2), 2857 (w), 1614 (w, val. arom. C=C), 1547 (s, δ–arom. C=C), 1475 (s, δ–CH_2), 1428 (vs, δ– CH_3), 1311 (m), 1248 (m), 1165 (s), 1137 (s), 1104 (m, val. arom. C-Cl), 1040 (m), 941 (w), 877 (w, δ–isol. arom–H), 790 (w), 724 (w), 609 (m).

MS (ESI): *m/z* (%): = double potassium salt: 929 (100) [M^+]
Dimer structures: $K_2M^+ \times$ 1KM : 1819 (100).

EA: $[C_{37}H_{50}Cl4K_2N_4O_6S_2]^+OH^-\cdot H_2O$ (965.89):
calc. C 46.01 H 5.53 N 5.80 Cl 14.68 S 6.64
found: C 45.81 H 5.75 N 5.64 Cl 14.72 S 6.31.

5.5.1.3. Bis-n-butyl–tetrabromo–trimethine

5,6–Dibromo–2–methyl–(1–H) benzimidazole (**95**)



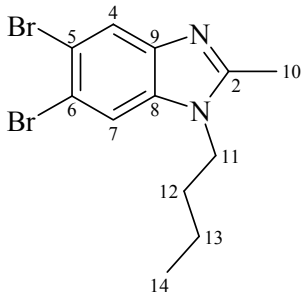
95

The synthesis of compound **95** followed the procedure given by Kihel *et al.*[115] To 13.5 g (0.1 mmol) of 1–H benzimidazole was added 150 mL of acetic acid and the compound was dissolved by heating the suspension at 60 °C. 37.5 g (210.0 mmol) of NBS was added in portions during 10 min under stirring. The solution was kept at that temperature for 5 h and cooled to room temperature. The product **95** precipitated on decreasing the temperature and was filtered off. Recrystallisation from toluene afforded compound **95** as light yellow prisms (yield 15.0 g, 51.7 mmol, 51 %, lit.[115] 62 %), m.p. 216 °C (lit.[115] 215-217 °C).

^{1}H NMR (acetone–d_6, 200.13 MHz): δ = 7.90 (s, 2 H, 4–, 7–H), 4.51 (s, 3 H, 10–H).

^{13}C NMR (acetone–d_6, 50.32 MHz): δ = 154.8 (s, C–8, –9), 139.5 (s, C–2), 119.1 (s, C–5, -6), 115.3 (d, C–4, –7), 14.8 (q, C–10).

1–Butyl–5,6–dibromo–2–methylbenzimidazole (**96**)



96

N–alkylation of intermediate **95** was performed analogously to Kyride *et al.*[116], but instead of aqueous NaOH, anhydrous K_2CO_3 was used. 8.6 g (29.66 mmol) of **95** and 5.3 g (38.35 mmol) of K_2CO_3 were suspended in 80 mL of *i*–PrOH. The temperature was increased to 80 °C and 5.30 g (38.7 mmol) of bromobutane was added dropwise during 30 min. The mixture was kept under reflux for 6 h and then cooled to room temperature and poured into 300 mL of water. The organic phase was extracted (3 × 150 mL) with EtOAc, washed with

200 mL of water and dried with Na_2SO_4. The solvent was removed by distillation and the residue chromatographed with $CHCl_3$/EtOAc/C_6H_{14} (5/3/2). Product **96** was obtained as white needles (8.00 g, 23.12 mmol, 78 %), m.p. 114 °C.

^{1}H NMR (acetone–d_6): δ = 7.91 (s, 1 H, 4–H), 7.89 (s, 1 H, 7–H), 4.26 (t, $^3J_{11,12}$ = 7.5 Hz, 2 H, 11–H), 4.59 (s, 3 H, 10–H), 1.81 (p, $^3J_{12,11}$ = 7.5 Hz, $^3J_{12,13}$ = 5.4 Hz, 2 H, 12–H), 1.43 (sx, $^3J_{13,12}$ = 5.2 Hz, $^3J_{13,14}$ = 7.4 Hz, 2 H, 13–H), 0.97 (t, $^3J_{14,13}$ = 7.4 Hz, 3 H, 14–H).

^{13}C NMR (acetone–d_6): δ = 155.2 (s, C–8), 144.6 (s, C–2), 136.9 (s, C–9), 123.8 (d, C–4), 116.6 (s, C–6), 116.4 (s, C–5), 115.3 (d, C–7), 44.4 (t, C–11), 34.5 (t, C–13), 20.6 (t, C–12), 14.0 (q, C–10), 13.9 (q, C–14).

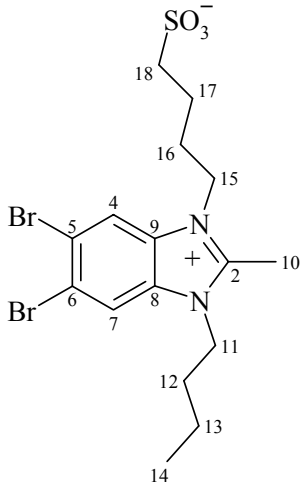
UV/vis (EtOH): λ_{max} (lg ε) = 242 nm (3.79), 292 (3.89), 300 (3.92).

IR[2] (KBr): $\tilde{\nu}$ = 3087 cm^{-1} (w, val. arom. C–H), 3054 (w), 3026 (w), 2959 (w, val. aliph. C–H, CH_3), 2924 (w, val. aliph. C–H, CH_2), 2864 (w), 1605 (w, val. arom. C=C), 1513 (s, δ–arom. C=C), 1461 (m, δ–CH_2), 1441 (s, δ–CH_3), 1389 (vs), 1362 (s), 1338 (w), 1303 (m), 1288 (w), 1242 (w), 1153 (w), 1121 (w), 1080 (m, val. arom. C–Br), 1036 (w, val. arom. C–Br), 1006 (w), 963 (w), 922 (w), 892 (s), 838 (m, δ–isol. arom–H), 791 (m), 775 (w), 749 (w), 693 (w), 666 (w), 646 (w), 584 (m), 561 (w).

MS (EI): *m/z* (%): = 346 (100) [M^+], 303 (93) [M–$C_3H_7^+$], 224 (29) [$K_{(303)}$–Br^+].

EA: $C_{12}H_{16}Br_2N_2$ (348.08): calc. C 41.65 H 4.08 N 8.09
found: C 41.44 H 4.05 N 8.01.

1–Butyl–5, 6–dibromo–2–methyl–3–(4–sulphobutyl) benzimidazoliumbetaine (**103**)



103

The betaine **103** was prepared analogously to compund **101**. 4.40 g (14.7 mmol) of benzimidazole **96** and 4.00 g (14.70 mmol) of 1,4–butanesultone **97b** were dissolved in 20 mL of chlorobenzene and the mixture was heated at 130 °C for 20 h. During this time the product **103** was filtered off every 3 h. Finally all fractions were combined, washed subsequently with acetone and ether and dried *in vacuo*. Recrystallisation from EtOH/water afforded pure **103** as white plates (6.02 g, 14.50 mmol, 98 %), m.p. > 320 °C.

^{1}H NMR (D_2O, 60°C): δ = 8.51 (s, 1 H, 4–H), 8.46 (s, 1 H, 7–H), 4.74 (s, 3 H, 10–H), 3.27 (t, $^3J_{11,\,12}$ = 7.5 Hz, 4 H, 11–, 15–H), 4.40 (p, $^3J_{12,\,11}$ = 7.5 Hz, $^3J_{12,\,13}$ = 7.7 Hz, 2 H, 12–H), 4.19 (m, 6 H, 16–, 17–, 18–H), 1.72 (sx, $^3J_{13,\,12}$ = 7.7 Hz, $^3J_{13,\,14}$ = 7.5 Hz, 2 H, 13–H), 1.27 (t, $^3J_{14,\,13}$ = 7.5 Hz, 3 H, 14–H).

^{13}C NMR (D_2O, 60°C): δ = 155.8 (s, C–2), 134.2 (s, C–8), 134.1 (s, C–9), 124.6 (s, C–6), 124.5 (s, C–5), 120.4 (d, C–4, –7), 53.2 (t, C–18), 49.0 (t, C–15), 48.6 (t, C–11), 33.4 (t, C-17), 30.2 (t, C–13), 24.5 (t, C–16), 24.3 (t, C–12), 15.9 (q, C–14, –10).

UV/vis (DMSO): λ_{max} (lg ε) = 254 nm (4.02), 260 (4.20), 290 (4.21), 298 (4.19sh).

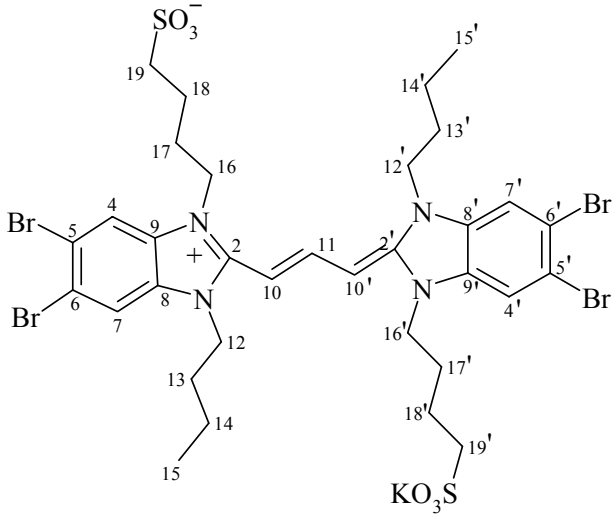
IR[2] (KBr): $\tilde{\nu}$ = 3097 cm^{-1} (w, val. arom. C–H), 3063 (w), 2996 (w), 2953 (w, val. aliph. C–H, CH_3), 2932 (w, val. aliph. C–H, CH_2), 2871 (w), 1597 (w, val. arom C=C), 1521 (w), 1461 (m, δ□CH_2), 1410 (w, δ–CH_3), 1376 (w), 1346 (w), 1299 (w), 1221 (w), 1181 (vs, val. asymm. SO_3^-), 1091 (w), 1057 (w), 1033 (s, val. symm. SO_3^-), 930 (w), 883 (w), 843 (m, δ–isol. arom–H), 778 (m), 752 (w), 598 (s).

MS (FAB+): *m/z* (%): = 483 (50) [M^+], 399 (1) [$(M–H_2SO_3)^+$], 154 (100).

EA: $C_{16}H_{22}Br_2N_2O_3S$ (484.23): calc. C 39.85 H 4.60 N 5.81

found: C 39.81 H 4.59 N 5.69

1–Butyl–2–{3–[1–butyl–5,6–dibromo–1,3–dihydro–3–(4–sulphobutyl) 2H–benzimidazol–2–ylidene]–1–propenyl} 5,6–dibromo–3–(4–sulphobutyl)–benzimidazole, inner salt, potassium salt (**106**)



106

For preparation of dye **106** the same method as for trimethine **104** was used. EtOH was used as solvent instead of MeOH. 3.00 g (6.22 mmol) of betaine **103** and 1.47 g (3.73 mmol) iodoform were mixed in 50 mL of EtOH. 1.70 g (15.2 mmol) of KO*t*-Bu was added in one portion under vigorous stirring. The reaction was carried out at ambient temperature for 3 h. The product was filtered off, washed with small amounts of water and acetone and recrystallised from DMF/water. Trimethine **106** was obtained as deep–violet crystals (0.90 g, 0.89 mmol, 28 %) after drying *in vacuo* (50 °C), m.p. (decomp.) 252–254 °C.

^{1}H NMR (DMSO–d_6): δ = 8.15 (s, 2 H, 4–, 4'–H), 8.08 (s, 2 H, 7–, 7'–H), 7.84 (t, $^3J_{11,\,10}$ = 13.4 Hz, 1 H, 11–H), 5.92 (d, $^3J_{10,\,11}$ = 13.3 Hz, 2 H, 10–, 10'–H), 4.30 (m, 8 H, 12–, 16–, 12'–, 16'–H), 4.50 (t, $^3J_{19,\,18}$ = 7.5 Hz, 4 H, 19–, 19'–H), 1.85 (m, 4 H, 13–, 13'–H), 1.72 (m, 8 H, 18–, 17–, 18'–, 17'–H), 1.35 (sx, $^3J_{14,\,13}$ = 7.6 Hz, $^3J_{14,\,15}$ = 7.3 Hz, 4 H, 14–, 14'–H), 0.91 (t, $^3J_{15,\,14}$ = 7.3 Hz, 6 H, 15–, 15'–H).

^{13}C NMR (DMSO–d_6): δ = 151.1 (s, C–2, –2'), 141.7 (d, C–11), 133.0 (s, C–8, –8'), 134.8 (s, C–9, –9'), 117.7 (s, C-6, –6'), 117.6 (s, C–5, –5'), 114.5 (d, C–4, –4'), 114.3 (d, C–7, –7'), 85.4 (d, C–10, –10'), 50.6 (t, C–19, –19'), 44.4 (t, C–16, –16'), 44.3 (t, C–12, –12'), 29.7 (t, C–14, –14'), 26.7 (t, C–17, 17'), 24.1 (t, C–18, –18'), 19.2 (t, C–13, –13'), 13.7 (q, C–15, –15').

UV/vis (DMSO): λ_{max} (lg ε) = 256 nm (14.09), 278 (4.01), 342 (3.56), 496 (4.83 sh), 530 (5.24).

UV/vis (EtOH): λ_{max} (lg ε) = 212 nm (4.84), 276 (3.97), 522 (5.11).

IR[2] (KBr): $\tilde{\nu}$ = 3097 cm^{-1} (w), 3030 (w, val. arom. C–H), 2955 (w, val. aliph. C–H, CH_3), 2923 (w, val. aliph. C–H, CH_2), 2868 (w), 2109 (w), 1608 (w, val. arom. C=C), 1552 (s, δ arom C=C), 1478 (s, δ–CH_2), 1429 (vs, δ–CH_3), 1314 (m), 1248 (w), 1204 (m), 1164 (vs, val. SO_3^-), 1035 (s, arom. C–Br), 944 (w), 853 (w), 820 (w, δ–isol. arom–H), 788 (w), 722 (m), 591 (s), 563 (m).

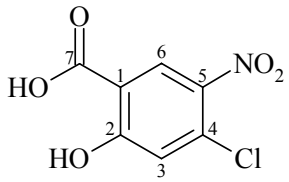
MS (FAB+): *m/z* (%): = 976 (23) [M^+]

EA: $C_{33}H_{41}Br_4KN_4O_6S_2 \cdot 1\ H_20$ (1030.57): calc. C 38.46 H 4.01 N 5.44
found: C 38.48 H 4.14 N 5.45.

5.5.2. Salicylic acid derivates of trimethines

5.5.2.1. *n*-Butyl–trimethine, salicylic acid derivatives

4–Chloro–5–nitrosalicylic acid (**109**)



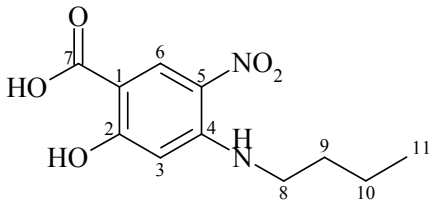
109

Compound **109** was synthesised by a way different from the route described in the literature.[121] 8.63 g (50.0 mmol) of 4–chlorosalicylic acid **108** was suspended in 60 mL of

acetic acid. Concentrated nitric acid (4 mL, 65 %, ρ = 1.40 g·(cm^3)$^{-1}$, 57.78 mmol) was carefully added dropwise during 15 min. The temperature increased to 70 °C without exterior heating and was kept there by heating for the next 1 h. The solution was poured into 200 mL of ice, filtered and dried *in vacuo*. The crude product (10.50 g, 48.3 mmol, 96 %), m.p. 196–198 °C, lit.[121]: 192 °C, was used without further purification.

^{1}H NMR (acetone–d_6, 200.13 MHz): δ = 10.22 (br. s, 2 H, COOH, ArOH), 8.46 (s, 1 H, 6-H), 7.12 (s, 1 H, 3–H).

4–*N*–Butylamino–5–nitrosalicylic acid (**110**)



110

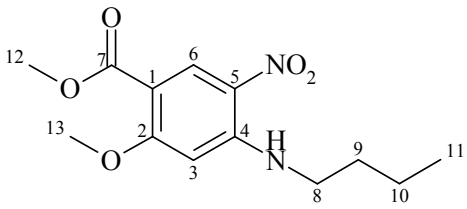
9.20 g (44.30 mmol) of **103**, 7.00 g (54.3 mmol) of EDPA and 3.65 g (50.0 mmol) of *n*-butylamine were dissolved in 50 mL of *i*–PrOH. The solution was kept under reflux for 45 h. After cooling to room temperature it was poured into 200 mL of ice and 10 mL of conc. HCl. The solid was filtered off and recrystallised from acetic acid. Aniline **110** was obtained as yellow prisms (5.80 g, 24.84 mmol, 54 %), m.p. 216–218 °C.

^{1}H NMR (DMSO–d_6): δ = 11.81 (br. s, 1 H, COOH), 8.58 (s, 1 H, 3–H), 8.37 (t, $^3J_{NH,\,8}$ = 5.6 Hz, 1 H, NH), 6.30 (s, 1 H, 6–H), 4.60 (br. s, 1 H, ArOH), 3.32 (d, $^3J_{8,\,NH}$ = 5.6 Hz, $^3J_{8,\,9}$ = 7.0 Hz, 2 H, 8–H), 1.61 (p, $^3J_{9,\,8}$ = 7.0 Hz, $^3J_{9,\,10}$ = 7.3 Hz, 2 H, 9–H), 1.39 (sx, $^3J_{10,\,9}$ = 7.3 Hz, $^3J_{10,\,11}$ = 7.5 Hz, 2 H, 10–H), 0.93 (t, $^3J_{11,\,10}$ = 7.5 Hz, 3 H, 11–H).

^{13}C NMR (DMSO–d_6): δ = 170.6 (s, C–7), 165.6 (s, C–2), 149.3 (s, C–5), 131.3 (d, C–6), 125.4 (s, C–4), 104.7 (s, C–1), 97.7 (d, C–3), 44.2 (t, C–8), 30.0 (t, C–10), 19.6 (t, C–9), 13.6 (q, C–11).

MS (EI): *m/z* (%): = 254 (28.3) [M^+], 211 (70.2) [M–$C_3H_7^+$], 193 (100) [$K_{(211)}$–H_2O^+], 175 (9.1) [$K_{(193)}$–H_2O^+].

Methyl–4–*N*–butylamino–2–methoxy–5–nitrobenzoate (**112**)



112

4.32 g (17.00 mmol) of **110**, 5.68 g (40.00 mmol) of methyliodide and 5.52 g (40.00 mmol) of anhydrous K_2CO_3 were suspended in 40 mL of DMF. The reaction was carried out for 5 h at 60 °C and the suspension was poured into 150 mL of ice and stirred for 2 h. The solid was filtered off and purified by recrystallisation from EtOH/HOAc. Product **112** appeared as lightly yellow polished plates (4.00 g, 14.20 mmol, 83 %), m.p. 130 °C.

^{1}H NMR ($CDCl_3$): δ = 8.83 (d, $^5J_{3,13}$ = 1.0 Hz, 1 H, 3–H), 8.44 (br. s, 1 H, NH), 6.11 (s, 1 H, 6–H), 3.97 (s, 3 H, 12–H), 3.85 (d, $^5J_{13,3}$ = 1.0 Hz, 3 H, 13–H), 3.32 (q, $^3J_{8,NH}$ = 7.3 Hz, $^3J_{8,9}$ = 6.6 Hz, 2 H, 8-H), 1.77 (p, $^3J_{9,8}$ = 6.6 Hz, $^3J_{9,10}$ = 7.4Hz, 2 H, 9–H), 1.51 (sx, $^3J_{10,9}$ = 7.4 Hz, $^3J_{10,11}$ = 7.3 Hz, 2 H, 10–H), 1.01 (t, $^3J_{11,10}$ = 7.3 Hz, 3 H, 11–H).

^{13}C NMR ($CDCl_3$): δ = 165.0 (s, C–7), 164.3 (s, C–2), 149.1 (s, C–5) 133.2 (d, C–6), 125.4 (s, C–4), 108.4 (s, C-1), 93.6 (s, C–3), 56.2 (q, C–12), 51.8 (q, C–13), 44.9 (t, C–8), 30.6 (t, C–10), 20.2 (t, C-9), 13.7 (q, C–11).

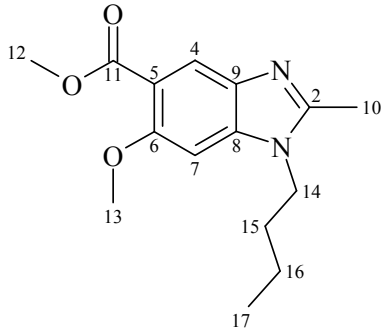
UV/vis ($CHCl_3$): λ_{max} (lg ε) = 240 nm (3.88), 276 (4.48), 312 (3.71 sh), 404 (3.79).

IR[2] (KBr): $\tilde{\nu}$ = 3358 cm^{-1} (m, val. sec. amine), 3104 (w, val. arom. C–H), 2981 (w), 2958 (m, val. aliph. C–H, CH_3), 2935 (m, val. aliph. C–H, CH_2), 2872 (m), 1695 (s, val. C=O), 1625 (vs, val. arom. C=C), 1569 (vs, val. asymm. NO_2), 1512 (s), 1471 (m, δ–CH_2), 1434 (s), 1411 (s, δ–CH_3), 1352 (s, val. symm. NO_2), 1303 (m), 1269 (m), 1239 (s, val. Ar–O–Me), 1212 (m), 1177 (w), 1132 (m, val. C–O), 1117 (m), 1086 (w), 1053 (m), 1003 (m), 961 (m), 939 (w), 868 (w), 819 (vs, δ–isol. arom–H), 803 (m), 780 (w), 755 (s), 688 (s), 597 (m), 556 (s).

MS (EI): *m/z* (%): = 282 (49.2) [M^+], 251 (15.7) [M–CH_3O^+], 239 (100) [M–$C_3H_7^+$], 221 (26.4) [$K_{(239)}$–H_2O^+], 211 (25.6) [$K_{(239)}$–CO^+], 179 (28.1) [$K_{(211)}$–CH_3OH^+].

EA: $C_{13}H_{17}N_2O_5$ (281.29): calc. C 55.51 H 6.09 N 9.96
found: C 55.32 H 6.38 N 9.70.

1–Butyl–6–methoxy–2–methyl–5–methylmethanoate–benzimidazole (**114**)



114

The benzimidazole **114** was synthesised as described above for compounds **91** and **93**. 3.60 g (14.77 mmol) of **112** and 5.90 g (90.0 mmol) of Zn–powder were suspended in 50 mL of toluene. 20 mL of acetic acid and 10 mL of acetic anhydride was added dropwise and the reaction mixture was heated for 40 h under reflux. After completion, the mixture was poured into 100 mL of ice–water and neutralised with 5 *N* NaOH solution. The organic phase was extracted with EtOAc (2 × 100 mL), washed with 100 mL of water and dried with $MgSO_4$. The solvents were evaporated *in vacuo* and the residue recrystallised from toluene: white needles (3.00 g, 10.90 mmol, 85 %), m.p. 107 °C.

^{1}H NMR ($CDCl_3$): δ = 8.13 (s, 1 H, 4–H), 6.75 (s, 1 H, 7–H), 4.05 (t, $^3J_{14,\,15}$ = 7.3 Hz, 2 H, 14–H), 3.95 (s, 3 H, 12–H), 3.91 (s, 3 H, 13–H), 4.58 (s, 3 H, 10–H), 1.77 (p, $^3J_{15,\,14}$ = 7.3 Hz, $^3J_{15,\,16}$ = 7.5 Hz, 2 H, 15–H), 1.39 (sx, $^3J_{16,\,15}$ = 7.5 Hz, $^3J_{16,\,17}$ = 7.4 Hz, 2 H, 16–H), 0.97 (t, $^3J_{17,\,16}$ = 7.4 Hz, 3 H, 17–H).

^{13}C NMR ($CDCl_3$): δ = 166.9 (s, C–11), 156.1 (s, C–8), 154.3 (s, C–6), 138.9 (s, C–2), 135.8 (s, C–9), 124.6, (d, C–4) 115.3 (s, C–5), 94.7 (d, C–7), 56.7 (q, C–12), 51.9 (q, C–13), 43.7 (t, C–14), 31.6 (t, C-16), 20.0 (t, C–15), 13.9 (q, C–17).

UV/vis ($CHCl_3$): λ_{max} (lg ε) = 242 nm (4.14), 260 (3.75 sh), 272 (3.559 sh), 306 (3.72).

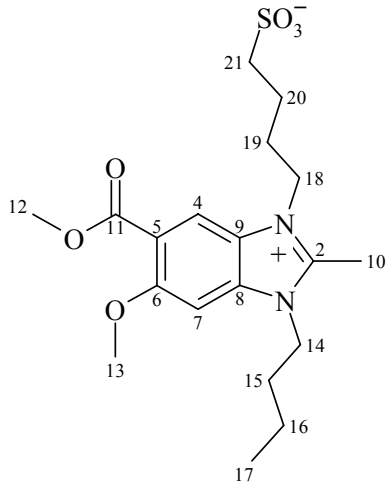
IR[2] (KBr): $\tilde{\nu}$ = 3026 cm^{-1} (w, val. arom. C–H), 2995 (w), 2951 (m, val. aliph. C–H, CH_3), 2929 (w, val. aliph. C–H, CH_2), 2869 (w), 2842 (w), 1689 (s, val. C=O), 1625 (s, val. arom. C=C), 1585 (w), 1526 (w), 1467 (m, δ–CH_2), 1438 (m, δ–CH_3), 1399 (s), 1359 (m), 1326

(w), 1249 (vs, val. Ar–O–Me), 1202 (m), 1113 (m, val. C–O), 1066 (m), 1026 (m), 1002 (w), 973 (w), 950 (w), 895 (m), 829 (m, δ–isol. arom–H), 781 (m), 706 (w), 653 (m).

MS (EI): *m/z* (%): = 276 (100) [M^+], 261 (30) [M–CH_3^+], 245 (90) [M–CH_3O^+], 233 (11) [M-$C_3H_7^+$].

EA: $C_{15}H_{20}N_2O_3$ (276.33): calc. C, 65.20; H, 7.30; N, 10.14
found: C, 65.22; H, 7.31; N, 10.05.

1–Butyl–6–methoxy–2–methyl–5–methylmethanoate–3–(4–sulphobutyl) benzimidazolium betaine (**116**)



116

The betaine **116** was obtained as previously described for **101** and **103**. Chlorobenzene was used as the solvent. 3.00 g (10.87 mmol) of **114** and 4.22 g (16.30 mmol) 1,4-butanesultone **97b** were dispersed in 10 mL of anhydrous solvent. The mixture was refluxed for 3 h and cooled to 10 °C. As a result a viscous mass appeared, that was recrystallised from EtOH: white prisms (3.20 g, 7.77 mmol, 71 %), m.p. 262 °C.

^{1}H NMR (DMSO–d_6): δ = 8.34 (s, 1 H, 4–H), 7.71 (s, 1 H, 7–H), 4.49 (m, 4 H, 14–, 18–H), 3.96 (s, 3 H, 12–H), 3.87 (s, 3 H, 13–H), 4.92 (s, 3 H, 10–H), 4.48 (t, $^3J_{21,\,20}$ = 7.5 Hz, 2 H, 21–H), 1.88 (p, $^3J_{20,\,21}$ = 7.5 Hz, $^3J_{20,\,19}$ = 7.2 Hz, 2 H, 20–H), 1.79 (p, $^3J_{19,\,20}$ = 7.2 Hz, $^3J_{19,\,18}$ = 7.5 Hz, 2 H, 19–H), 1.73 (p, $^3J_{15,\,14}$ = 7.6 Hz, $^3J_{15,\,16}$ = 7.5 Hz, 2 H, 15–H), 1.40 (sx, $^3J_{16,\,15}$ = 7.5 Hz, $^3J_{16,\,17}$ = 7.5 Hz, 2 H, 16–H), 0.94 (t, $^3J_{17,\,16}$ = 7.5 Hz, 3 H, 17–H).

^{13}C NMR (DMSO–d_6): δ= 165.6 (s, C–11), 156.6 (s, C–8), 154.4 (s, C–6), 133.6 (s, C–2), 124.1 (s, C–9), 120.2 (s, C–5), 115.0 (d, C–4), 96.2 (d, C–7), 57.0 (q, C–12), 54.4 (q, C–13), 50.4 (t, C–21), 44.9 (t, C–18), 44.8 (t, C–14), 30.4 (t, C–16), 27.6 (t, C–20), 24.0 (t, C–19), 19.1 (t, C–15), 13.5 (q, C–10), 10.5 (q, C–17).

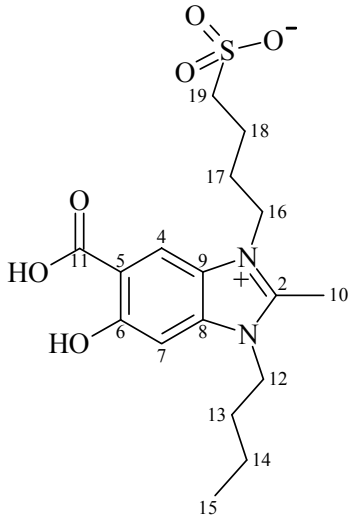
UV/vis (DMSO): λ_{max} (lg ε) = 264 nm (3.74), 302 (3.90).

IR[2] (KBr): $\tilde{\nu}$ = 3508 cm^{-1} (m), 3451 (m), 3306 (w), 3131 (w), 3061 (w, val. arom. C–H), 2940 (m, val. aliph. C–H, CH_3), 2874 (w), 2842 (w), 1725 (s, val. C=O), 1635 (m, val. arom. C=C), 1545 (m), 1515 (m), 1483 (s), 1455 (m, δ–CH_2), 1434 (s, δ–CH_3), 1377 (w), 1356 (w), 1233 (s, val. Ar–O–Me), 1211 (s), 1163 (vs, val. asymm. SO_3^-), 1083 (m, val. C–O), 1060 (m), 1029 (vs, val. symm. SO_3^-), 1014 (s), 924 (w), 887 (m), 849 (m, δ–isol. arom–H), 781 (s), 749 (m), 705 (m), 601 (s).

MS (ESI): *m/z* (%): = 863 (4) [2M+K^+], 825 (7) [2M+H^+], 451 (40) [M+K^+], 413 (100) [M+H^+].

EA: $C_{19}H_{28}N_2O_6S$ (414.50): calc. C 55.32 H 6.84 N 6.79
found: C 54.66 H 7.00 N 6.64.

1–Butyl–5–carboxyloxy–6–hydroxy–2–methyl–3–(4–sulphobutyl)benzimidazoliumbetaine (**118**)



118

Deprotection of both methyl–groups was carried out analogously to Nakazawa and Sawahara.[126] 3.20 g (7.77 mmol) of **116** was refluxed for 48 h in 16 mL of 48 % HBr and 8 mL of water. After completion of the reaction, the water was almost distilled off, the residue cooled to room temperature and boiled in 20 mL of acetone. **118** was obtained as white plates (4.65 g, 5.70 mmol, 73. %), m.p. 310 °C.

^{1}H NMR (DMSO–d_6): δ = 11.2 (br. s, 1 H, COOH), 8.49 (s, 1 H, 4–H), 7.57 (s, 1 H, 7–H), 5.02 (br. s, ArOH), 4.51 (t, $^3J_{16,\,17}$ = 7.4 Hz, 2 H, 16–H), 4.40 (t, $^3J_{12,\,13}$ = 7.4 Hz, 2 H, 12–H), 4.92 (s, 3 H, 10–H), 4.57 (t, $^3J_{19,\,18}$ = 7.5 Hz, 2 H, 19–H), 1.88 (m, 2 H, 18–H), 1.74 (m, 4 H, 17–, 13–H), 1.37 (sx, $^3J_{14,\,13}$ = 7.6 Hz, $^3J_{14,\,15}$ = 7.3 Hz, 2 H, 14–H), 0.94 (t, $^3J_{15,\,14}$ = 7.3 Hz, 3 H, 15–H).
^{13}C NMR (DMSO–d_6): δ = 171.5 (s, C–11), 159.1 (s, C–8), 153.8 (s, C–6), 135.6 (s, C–2), 123.9 (s, C–9), 115.4 (s, C–5), 114.2 (d, C–4), 99.4 (d, C–7), 79.0 (t, C–19), 50.4 (t, C–16), 45.0 (t, C–12), 30.4 (t, C-14), 27.5 (t, C–18), 21.9 (t, C–17), 19.2 (t, C–13), 13.6 (q, C–10), 10.6 (q, C–15).

UV/vis (DMSO): λ_{max} (lg ε) = 270 nm (4.20), 276 (4.20), 364 (3.12 sh).

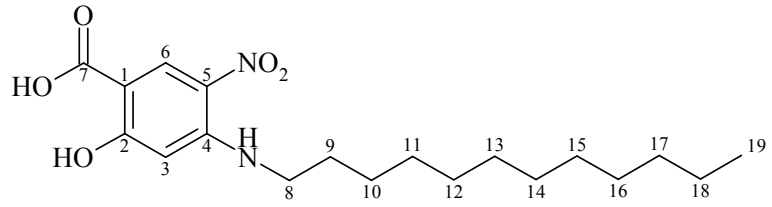
IR[2] (KBr): $\tilde{\nu}$ = 3314 cm^{-1} (m, val. ArO–H, ArOH:::HOOC), 3037 (w, val. arom. C–H), 2966 (m), 2929 (m, val. aliph. C–H, CH_3), 2832 (m, val. aliph. C–H, CH_2), 1679 (vs, val. C=O), 1640 (s, val. C=O:::HO), 1611 (m, val. arom. C=C), 1545 (m), 1513 (m), 1471 (s, δ–CH_2), 1443 (s), 1412 (vs, δ–CH_2), 1383 (s, δ–OH), 1286 (w), 1240 (m), 1203 (s), 1165(vs, val. asymm. SO_3^-), 1133 (vs, val. C–O), 1031 (s, val. symm. SO_3^-), 940 (m), 873 (m), 827 (s, δ–isol. arom–H), 789 (m), 755 (s), 723 (s), 583 (s), 551 (s).

MS (ESI): *m/z* (%): = 791 (8) [2M+Na^+], 769 (29) [2M+H^+], 385 (100) [M+H^+], 367 (5) [M-OH^+].

EA: $C_{17}H_{24}N_2O_6S$ (384.45): calc. C 53.11 H 6.29 N 7.29
found: C 53.10 H 6.31 N 6.99.

5.5.2.2. *n*-Dodecyl–trimethine, salicylic acid derivatives

4–*N*–Dodecyl–5–nitrosalicylic acid (**111**)



111

The synthesis of compound **111** was carried out as described above for **110**. 4.40 g (20.20 mmol) of **109** and 3.87 g (30.0 mmol) of EDPA were dissolved in 40 mL of *i*–PrOH. 4.3 g (23.10 mmol) of dodecylamine were added in one portion and the solution was kept under reflux for 100 h. The reaction solution was poured into 200 mL of ice–water–conc. HCl (40 mL) and the solid was filtered off. Recrystallisation from MeOH afforded the aniline **111** as dark–yellow needles (3.72 g, 10.16 mmol, 50 %), m.p. 130 °C.

^{1}H NMR (DMSO–d_6): δ = 11.97 (s, 1 H, COO<u>H</u>), 8.59 (s, 1 H, 3–H), 8.38 (t, $^3J_{\underline{NH},\,8}$ = 5.8 Hz, 1 H, N<u>H</u>), 6.29 (s, 1 H, 6–H), 3.89 (br. s, 1 H, ArO<u>H</u>), 3.31 (q, $^3J_{8,\,\underline{NH}}$ = 5.8 Hz, $^3J_{8,\,9}$ = 6.8 Hz, 2 H, 8–H), 1.60 (p, $^3J_{9,\,8}$ = 6.8 Hz, $^3J_{9,\,10}$ = 7.4 Hz, 2 H, 9–H), 1.32 (m, 2 H, 10–H), 1.23 (s, 16 H, 11–, 12–, 13–, 14–, 15–, 16–, 17–, 18–H), 0.85 (t, $^3J_{19,\,18}$ = 7.1 Hz, 3 H, 19–H).

^{13}C NMR (DMSO–d_6): δ = 170.6 (s, C–7), 165.7 (s, C–2), 149.3 (s, C–5), 131.2 (d, C–6), 125.4 (s, C–4), 104.7 (s, C–1), 97.6 (d, C–3), 44.4 (t, C–8), 38.9 (t, C–9), 31.2 (t, C–13), 28.98 (t, C–12), 28.96 (t, C-11), 28.90 (t, C–10), 28.87 (t, C–14), 28.99 (t, C–15), 27.8 (t, C-16), 26.3 (t, C–18), 24.0 (t, C–17), 13.9 (q, C–19).

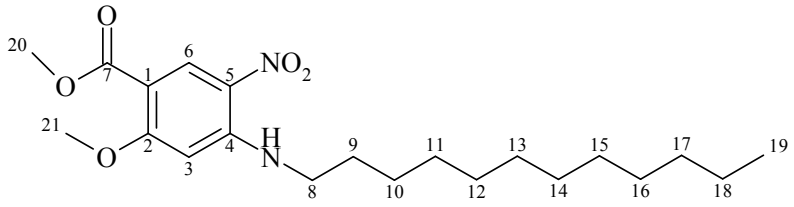
UV/vis (DMSO): λ_{max} (lg ε) = 254 nm (4.08), 278 (4.39), 402 (3.87).

IR[2] (KBr): $\tilde{\nu}$ = 3356 cm^{-1} (w, val. ArO–H), 2980 (w, val. arom. C–H), 2951 (w), 2931 (w, val. aliph. C–H, CH_3), 2914 (m), 2848 (m, val. aliph. C–H, CH_2), 1661 (s, val. C=O), 1641 (s, val. C=O:::HO), 1547 (w, val. C=C), 1514 (m), 1444 (m, δ–CH_2), 1413 (s, δ–CH_3), 1384 (m, val. symm. NO_2), 1242 (w), 1204 (m), 1152 (m), 1123 (m), 1061 (w), 1035 (m), 921 (m), 875 (w), 831 (m, δ–isol. arom–H), 790 (m), 756 (s), 699 (vs), 608 (m), 575 (vs), 561 (s).

MS (EI): *m/z* (%): = 366 (11) [M^+], 349 (11) [$M–OH^+$], 331 (39) [$K_{(349)}–H_2O^+$], 311 (41) [$K_{(331)}–H_2O^+$], 287 (9) [$K_{(331)}–C_3H_8^+$], 211 (100) [$M–C_{11}H_{23}^+$], 193 (96) [$K_{(211)}–H_2O^+$].

EA: $C_{19}H_{30}N_2O_5$ (366.45): calc. C 64.28 H 8.25 N 7.64
found: C 64.28 H 8.56 N 7.77.

Methyl–4–*N*–dodecyl–2–methoxy–5–nitrobenzoate (**113**)



113

Protection of the salicylic acid hydroxyl groups was performed as described above for compound **55**: 3.20 g (8.75 mmol) of **60**, 4.76 g (20.0 mmol) of K_2CO_3 and 4.84 g (20.0 mmol) of methyliodide were suspended in 30 mL of DMF and the mixture was heated to 60 °C for 5 h. After completion of the reaction, the mixture was poured into 100 mL of ice–water. The solid was filtered off, washed subsequently with 200 mL of water, 100 mL of 10% acetic acid, 100 mL of water and 20 mL of cold MeOH. Recrystallisation from EtOH afforded **61** as light–yellow plates (3.00 g, 7.61 mmol, 87 %), m.p. 114 °C.

^{1}H NMR ($CDCl_3$): δ = 8.84 (s, 1 H, 3–H), 8.45 (br. s, 1 H, NH), 6.11 (s, 1 H, 6–H), 3.97 (s, 3 H, 20–H), 3.85 (s, 3 H, 21–H), 3.31 (q, $^3J_{8,\,NH}$ = 5.2 Hz, $^3J_{8,\,9}$ = 6.8 Hz, 2 H, 8–H), 1.77 (p, $^3J_{9,\,8}$ = 6.8 Hz, $^3J_{9,\,10}$ = 7.2 Hz, 2 H, 9–H), 1.47 (m, 2 H, 10–H), 1.35 (m, 2 H, 11–H), 1.27 (s, 14 H, 12–, 13–, 14–, 15–, 16–, 17–, 18–H), 0.88 (t, $^3J_{19,\,18}$ = 7.0 Hz, 3 H, 19–H).

^{13}C NMR ($CDCl_3$): δ = 165.1 (s, C–7), 164.3 (s, C–2), 149.2 (s, C–5), 133.3 (d, C–6), 125.5 (s, C–4), 108.5 (s, C–1), 93.7 (d, C–3), 56.3 (q, C–20), 51.8 (q, C–21), 43.3 (t, C–8), 31.9 (t, C–9), 29.60 (t, C–13), 29.59 (t, C–12), 29.52 (t, C–11), 29.45 (t, C–10), 29.30 (t, C–14), 29.24 (t, C–15), 28.6 (t, C–16), 27.0 (t, C–18), 24.7 (t, C–17), 14.1 (q, C–19).

UV/vis ($CHCl_3$): λ_{max} (lg ε) = 240 nm (4.02), 276 (4.56), 312 (3.84 sh), 404 (3.92).

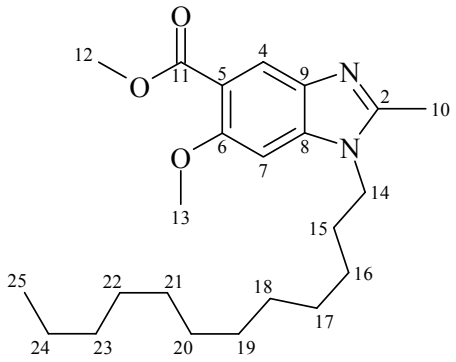
IR[2] (KBr): $\tilde{\nu}$ = 3367 cm^{-1} (w), 3164 (w), 3034 (w, val. arom. C–H), 2981 (w), 2932 (w, val. aliph. C-H, CH_3), 2914 (m, val. aliph. C–H, CH_2), 2873 (w), 2850 (m), 1691 (s, val. C=O),

1636 (m), 1613 (w, val. C=C), 1566 (w), 1548 (w), 1514(w), 1471 (w, δ–CH_2), 1412 (s, δ–CH_3), 1357 (m, val. symm. NO_2), 1242 (m, val. Ar–O–Me), 1223 (m), 1204 (m), 1167 (m), 1129 (m, val. C–O), 1063 (m), 1034 (m), 1004 (s), 959 (m), 940 (m), 873 (w), 816 (s, δ–isol. arom–H), 756 (s), 713 (s), 689 (s), 575 (vs).

MS (EI): *m/z* (%): = 394 (39) [M^+], 377 (14.6) [M–OH^+], 364 (15) [M–$HCHO^+$], 359 (75) [$K_{(377)}$–H_2O^+], 239 (100) [M–$C_{11}H_{23}^+$], 208 (33) [$K_{(239)}$–CO^+].

EA: $C_{21}H_{34}N_2O_5$ (394.51): calc. C 63.94 H 8.69 N 7.10
found: C 63.88 H 8.88 N 6.93.

1–Dodecyl–6–methoxy–2–methyl–5–methylmethanoatebenzimidazole (**115**)



115

The synthesis of **115** was performed using the method presented for compound **114**. 4.10 g (5.30 mmol) of aniline **113** and 1.57 g (24.00 mmol) of Zn–powder were dispersed in 20 mL of dry toluene. The suspension was heated to 100 °C and 10 mL of acetic acid was added dropwise carefully during 30 min. In 1 hour 5 mL of acetic anhydride was poured into the mixture, while it was refluxed for 20 h. After cooling to room temperature the reaction mixture was poured into 200 mL of ice–water, neutralised with 25 % ammonia and extracted with EtOAc (3 × 100 mL). The organic phase was washed with copiuos amounts of water, dried with $MgSO_4$ and the solvent was removed by distillation. The residue was frozen in liquid nitrogen and 10 mL of cold hexane was added. The solid was quickly filtered off on a cooled funnel. Product **115** appeared as dirty white plates, which turned into heavy oil at ambient temperature (4.00 g, 5.15 mmol, 97 %).

^{1}H NMR ($CDCl_3$): δ = 8.13 (s, 1 H, 4–H), 6.76 (s, 1 H, 7–H), 4.05 (t, $^3J_{14,\,15}$ = 7.4 Hz, 2 H, 14–H), 3.96 (s, 3 H, 12–H), 3.90 (s, 3 H, 13–H), 4.59 (s, 3 H, 10–H), 1.78 (p, $^3J_{15,\,14}$ = 7.4 Hz,

$^{3}J_{15,16}$ = 7.1 Hz, 2 H, 15–H), 1.33 (m, 2 H, 16–H), 1.25 (s, 16 H, 17–, 18–, 19–, 20–, 21–, 22–, 23–, 24–H), 0.88 (t, $^{3}J_{25,24}$ = 6.7 Hz, 3 H, 25–H).

^{13}C NMR ($CDCl_3$): δ = 166.9 (s, C–11), 156.2 (s, C–8), 154.3 (s, C–6), 138.4 (s, C–2), 138.4 (s, C–9), 124.6 (s, C–5), 124.0 (d, C–4), 94.8 (d, C–7), 56.8 (q, C–12), 51.9 (q, C–13), 44.0 (t, C–14), 31.9 (t, C–15), 29.54 (t, C–19), 29.49 (t, C–18), 29.41 (t, C–17), 29.28 (t, C–16), 29.20 (t, C–20), 27.0 (t, C–21), 26.9 (t, C–22), 24.6 (t, C–24), 21.0 (t, C–23), 14.0 (q, C–25).

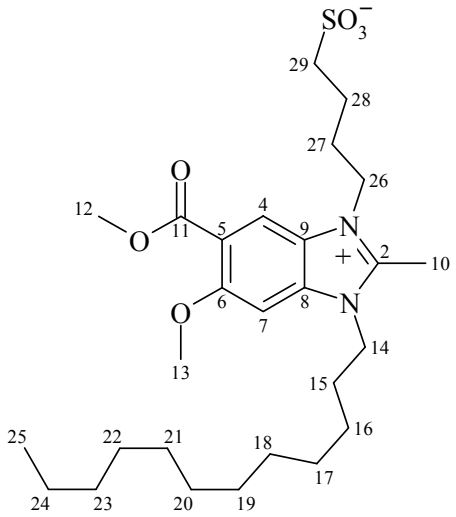
UV/vis ($CHCl_3$): λ_{max} (lg ε) = 242 nm (4.22), 258 (3.79 sh), 272 (3.63 sh), 306 (3.75).

IR[2] (KBr): $\tilde{\nu}$ = 3589 cm^{-1} (w), 3394 (w), 2923 (s, val. aliph. C–H, CH_3), 2853 (m, val. aliph. C–H, CH_2), 1723 (s, val. C=O), 1628 (s, val. arom. C=C), 1587 (w), 1528 (w), 1466 (s, δ–CH_2), 1433 (s, δ–CH_3), 1398 (s), 1362 (m), 1328 (w), 1249 (s, val. Ar–O–Me), 1230 (vs), 1188 (s, val. asymm. SO_3^-), 1114 (m, val. C–O), 1069 (s, val. symm. SO_3^-), 1022 (w), 1000 (w), 967 (w), 901 (w), 810 (m, δ–isol. H–arom.), 785 (m), 723 (w), 655 (w).

MS (EI): *m/z* (%): = 388 (100) [M^+], 373 (94) [M–CH_3^+], 357 (41) [M–CH_3O^+], 345 (24) [M-$C_3H_7^+$], 331 (30) [M–$C_4H_9^+$], 303 (30) [M–$C_6H_{13}^+$], 234 (74) [M–$C_{11}H_{22}^+$].

EA: $C_{23}H_{36}N_2O_3 \cdot 0.5\ H_2O$ (397.57): calc. C 69.49 H 9.13 N 7.05
found: C 69.16 H 9.28 N 6.94.

1–Dodecyl–6–methoxy–2–methyl–5–methylmethanoate–3–(4–sulphobutyl) benzimidazolium betaine (**117**)



117

Quaternisation of compound **115** was performed as described for betaine **116**: 1.27 g (3.28 mmol) of benzimidazole **115** and 0.50 g (3.68 mmol) of 1,4–butanesultone **97b** were refluxed for 10 h in 10 mL of chlorobenzene. After cooling to 10 °C 30 mL of ether added and the product precipitated. The flask was placed in the refrigerator for 2 d and the solid was filtered off. Product **117** was obtained as white plates (1.48 g, 4.82 mmol, 86 %), m.p. 198–200 °C.

^{1}H NMR (DMSO–d_6): δ = 8.33 (s, 1 H, 4–H), 7.69 (s, 1 H, 7–H), 4.46 (q, $^{3}J_{14,\,15}$ = 7.6 Hz, $^{3}J_{26,\,27}$ = 7.9 Hz, 4 H, 14–, 26–H), 3.95 (s, 3 H, 12–H), 3.86 (s, 3 H, 13–H), 4.91 (s, 3 H, 10-H), 4.48 (t, $^{3}J_{29,\,28}$ = 7.5 Hz, 2 H, 29–H), 1.87 (p, $^{3}J_{28,\,29}$ = 7.5 Hz, $^{3}J_{28,\,27}$ = 7.8 Hz, 2 H, 28–H), 1.78 (p, $^{3}J_{27,\,28}$ = 7.8 Hz, $^{3}J_{27,\,26}$ = 7.9 Hz, 2 H, 27–H), 1.68 (p, $^{3}J_{15,\,14}$ = 7.6 Hz, $^{3}J_{15,\,16}$ = 7.3 Hz, 2 H, 15–H), 1.33 (m, 4 H, 16–, 17–H), 1.23 (s, 14 H, 18–, 19–, 20–, 21–, 22-, 23–, 24–H), 0.85 (t, $^{3}J_{25,\,24}$ = 7.0 Hz, 3 H, 25–H).

^{13}C NMR (DMSO–d_6): δ = 165.5 (s, C–11), 156.5 (s, C–8), 154.4 (s, C–6), 133.6 (s, C–2) 124.1 (s, C–9), 120.2 (s, C–5), 115.0 (d, C–4), 96.2 (d, C–7), 57.0 (q, C–12), 54.4 (q, C–13), 50.3 (t, C–29), 44.9 (t, C–14, –26), 38.9 (t, C–15), 31.2 (t, C–19), 28.93 (t, C–18), 28.90 (t, C–17), 28.87 (t, C–16), 28.81 (t, –20), 28.59 (t, C–21), 28.56 (t, C–22), 28.29 (t, C–24), 27.5 (t, C–28), 25.7 (t, C-27), 24.0 (t, C–23), 13.8 (q, C–10), 10.4 (q, C–25).

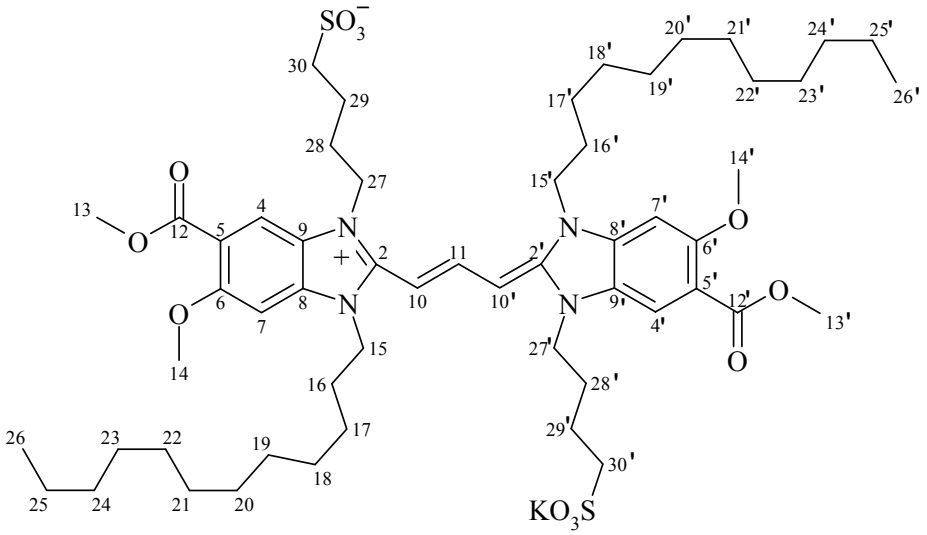
UV/vis (DMSO): λ_{max} (lg ε) = 266 nm (3.93), 294 (3.95), 374 (2.86 sh).

IR[2] (KBr): $\tilde{\nu}$ = 3031 cm^{-1} (w, val. arom. C–H), 2919 (m, val. aliph. C–H, CH_2), 2850 (m), 1724 (m, val. C=O), 1636 (w, val. C=C), 1548 (w), 1517 (w), 1481 (m), 1440 (m, δ–CH_2), 1418 (m, δ–CH_3), 1383 (w), 1222 (m, val. Ar–O–Me), 1162 (s, val. asymm. SO_3^-), 1085 (m, val. C-O), 1030 (vs, val. symm. SO_3^-), 938 (w), 828 (w, δ–isol. arom–H), 779 (m), 753 (w), 713 (m), 665 (w), 596 (s), 573 (w).

MS (ESI): *m/z* (%): = 563 (>0.1) [M+K^+], 525 (>0.1) [M+H^+], 388 (99) [M–$C_4H_8SO_3^+$], 373 (100) [$K_{(388)}$–CH_3^+], 234 (86) [$K_{(388)}$–$C_{11}H_{22}^+$].

EA: $C_{27}H_{44}N_2O_6S$ (524.72): calc. C 61.80 H 8.45 N 5.34
found: C 61.72 H 8.58 N 5.33.

1–Dodecyl–2–{3–[1–dodecyl–6–methoxy–5–methylmethanoate–1,3–dihydro–3–(4–sulphobutyl) 2H–benzimidazol–2–ylidene]–1–propenyl} 6–methoxy–5–methylmethanoate–3–(4–sulphobutyl)–benzimidazole, inner salt, potassium salt (**120**)



120

The synthesis of trimethine **120** followed the preparative method for dye **104**. 0.636 g (1.21 mmol) of betaine **117** and 0.24 g (0.61 mmol) of iodoform were suspended in 10 mL of MeOH. 0.34 g (3.00 mmol) of KO*t*-Bu was added in one portion under vigorous stirring. The reaction was carried out for 2 h at ambient temperature and half of the solvent was distilled off under reduced pressure. The flask was placed in the refrigerator for 2 d. The precipitated

solid was filtered off and chromatographed with MeOH/$CHCl_3$ (1:1). The dye **120** was obtained as deep red plates (0.20 g, 0.19 mmol, 31 %), m.p. (decomp.) 292 °C.

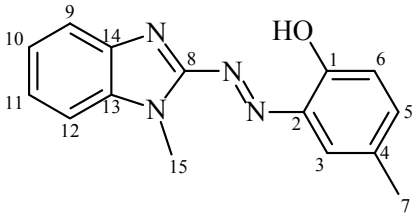
^{1}H NMR (DMSO–d_6): δ = 7.86 (s, 2 H, 4–, 4'–H), 7.85 (t, $^3J_{11, 10}$ = 13.0 Hz, 1 H, 11–H), 7.35 (s, 2 H, 7–, 7'–H), 5.86 (d, $^3J_{10, 11}$ = 13.0 Hz, 2 H, 10–, 10'–H), 4.38 (t, $^3J_{27, 28}$ = 6.6 Hz, 4 H, 27–, 27'–H), 4.29 (t, $^3J_{15, 16}$ = 6.6 Hz, 4 H, 15–, 15'–H), 3.92 (s, 6 H, 13–, 13'–H), 3.84 (s, 6 H, 14–, 14'–H), 4.54 (t, $^3J_{30, 29}$ = 7.4 Hz, 4 H, 30–, 30'–H), 1.86 (m, 4 H, 29–, 29'–H), 1.78 (m, 4 H, 28–, 28'–H), 1.71 (m, 4 H, 16–, 16'–H), 1.23 (m, 8 H, 18–, 17–, 18'–, 17'–H), 1.17 (s, 28 H, 19–, 20–, 21–, 22–, 23–, 23–, 24–, 25–, 19'–, 20'–, 21'–, 22'–, 23'–, 24'–, 25'–H), 0.82 (t, $^3J_{26, 25}$ = 6.9 Hz, 6 H, 26'–, 26–H).

^{13}C NMR (DMSO–d_6): δ = 167.9 (s, C–12, –12'), 165.9 (s, C–8, –8'), 163.8 (s, C–2, –2'), 148.9 (s, C–6, –6'), 141.1 (d, C–11), 123.2 (s, C–5, –5'), 119.9 (d, C–4, –4'), 94.5 (d, C–7, -7'), 85.0 (d, C–10, –10'), 56.9 (q, C–13, –13'), 54.0 (q, C–14, –14'), 50.7 (t, C–30, –30'), 44.2 (t, C–15, –27, –15', -27'), 38.9 (t, C–16, –16'), 31.2 (t, C–19, –20, –19', –20'), 28.9 (t, C–18, -17, –18', –17'), 28.8 (t, C-21, –22, –21', –22'), 28.6 (t, C–23, –29, –23', –29'), 25.8 (t, C–25, -25'), 24.0 (t, C–24, –28, –24', –28'), 13.8 (q, C–26, –26').

MS (EI): *m/z* (%): = 1103 (100) [$(Na^+M^-)Na^+$], 1081 (21) [$(Na^+M^-)^+$], 1059 (25) [$(M+H)^+$].

5.6. Complex–forming azo dyes

4–Methyl–2–(1–methylbenzimidazol–2–ylazo) phenol (**122**)



122

The dye **122** was synthesised according to Kolodjajnaja *et al.*[131] 0.9 g (6.10 mmol) of 2-amino–1–methylbenzimidazole **121** was dissolved in 10 mL of conc. phosphoric acid (65 %) and the mixture was precooled to –15 °C by means of an ice/NaCl cooling bad. 0.60 g

(8.70 mmol) of solid $NaNO_2$ was slowly added for 1 h. The reaction solution was stirred for additional 2 h and at this temperature slowly poured into 20 mL of acetic acid solution of 0.66 g (6.1 mmol) *p*–cresol at 0–5 °C and stirred for 3 h. After completion, the reaction solution was neutralised with NaOH solution, the solid was filtered off, and the filtrate was extracted (3 × 100 mL) with ether, dried with Na_2SO_4 and the solvent was evaporated *in vacuo*. The combined products were purified by FC (Tol/EtOH–8/1) and by recrystallisation from EtOH: red–brown needles (0.53 g, 2.0 mmol, 33 %, lit.[131]: 18 %), m.p. 196 °C, (lit.[131]: 196–197 °C).

^{1}H NMR (DMSO–d_6): δ = 7.45 (dd, $^3J_{11,12}$ = 9.0 Hz, 2 H, 10–, 11–H), 7.61 (d, $^4J_{3,5}$ = 1.3 Hz, 1 H, 3–H), 7.40 (dd, $^3J_{5,6}$ = 8.2 Hz, $^4J_{5,3}$ = 1.2 Hz, 1 H, 5–H), 7.34 (dd, $\Sigma_{J\,12,11}$ = 16.2 Hz, 2 H, 12–, 9–H), 7.04 (d, $^3J_{6,5}$ = 8.4 Hz, 1 H, 6–H), 4.14 (s, 3 H, 15–H), 4.31 (s, 3 H, 7–H).

^{13}C NMR (DMSO–d_6): δ = 155.05 (s, C–13), 154.99 (s, C–1), 141.6 (s, C–8), 140.1 (s, C–2), 136.3 (d, C–5), 135.9 (s, C–14), 128.6 (d, C–4), 124.0 (d, C–11), 123.4 (d, C–10), 120.4 (d, C–3), 119.0 (d, C–12), 118.5 (d, C–9), 111.0 (d, C–6), 30.2 (q, C–15), 20.0 (q, C–7).

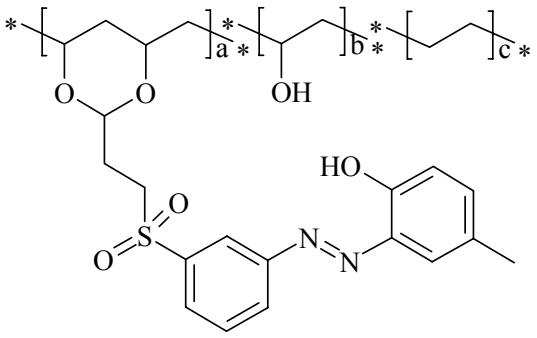
UV/vis (EtOH):λ_{max} (lg ε) = 206 nm (4.36), 298 (3.45 sh), 382 (4.03), 438 (4.11), 478 (4.01 sh), 502 (3.82)

IR[1] (KBr): $\tilde{\nu}$ = 3261 cm^{-1} (w, val. arom. O–H), 3056 (w, val. arom. C–H), 3025 (w), 2917 (w, val. aliph. C–H, CH_3), 2860 (w), 1615 (m, val. arom. C=C), 1588 (m), 1504 (s), 1486 (s), 1433 (m, δ–CH_3), 1392 (m), 1374 (m), 1331 (m), 1278 (m), 1257 (m), 1230 (s), 1209 (m), 1193 (m), 1178 (m), 1140 (s, val. C–O), 1115 (m), 819 (m, two neighbours arom. H–atoms), 811 (m, isol. arom. H–atom), 743 (m, four neighbours arom. H–atoms), 733 (m), 708 (w), 569 (w)

MS (EI): *m/z* (%): =266 (82) [M^+], 251 (3) [M–CH_3^+], 249 (10) [M–OH^+], 238 (77) [M-CO^+], 237 (100) [M–CHO^+].

5.7. Dyes covalently bound to polymers

Poly(vinyl{3–[3–(2–hydroxi–5–methyl)phenylazo]sulphonophenylpropanal}*co*-vinyl alcohol *co*-ethylen) (**50**)

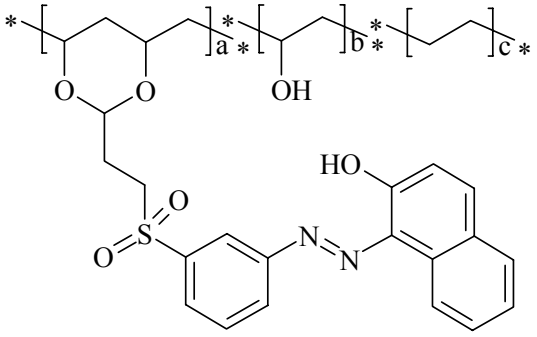


50

The dye **19** was covalently bound to the poly(vinyl alcohol *co*-ethylen) (27 mol % ethylene content) according to **G. Pr. 4.2.5.** 0.04 g (0.12 mmol) of **19** and 0.40 g (app. 10.11 mmol) of PVA *co* PE were dissolved in 20 mL of DMF at 70 °C. 1 mL of conc. HCl (37 %) was added and the reaction was carried out at that temperature for 2 h. After the purification described above the dye–polymer was dried *in vacuo* for 5 h. Composite **50** appeared as a yellow polymer, no dye spots were noticed by TLC analysis (yield 0.30 g, 68 %).

UV/vis (DMSO, 1.347 mg/10 mL): λ_{max} (a.u.) = 257 nm (0.549), 286 (0.528), 321 (0.504), 398 (0.268).

Poly(vinyl{3–[3–(2–hydroxinaphthylazo]sulphonophenylpropanal}*co*-vinyl alcohol *co*-ethylen) (**51**)



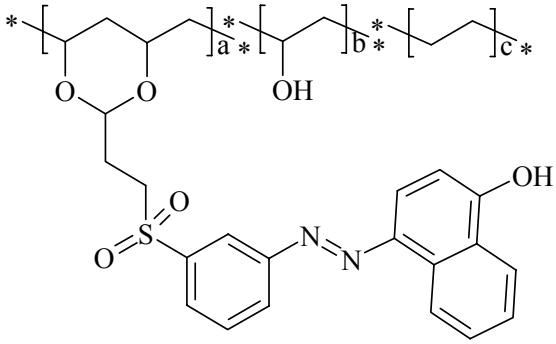
51

The polymer **51** was synthesised according to **G. Pr. 4.2.5**: 0.40 g (0.11 mmol) of aldehyde **44** and 0.42 g (app. 10.6 mmol, containing ca. 7.75 mmol OH–groups) PVA *co* PE (27.0

mol %) were dissolved in 30 mL of DMF. The solvent was heated to 75 °C and 1 mL of conc. HCl (37 %) was added. After 3.5 h TLC (acetone) monitoring shows, that no more free dye is presented in the reaction mixture. The solution was poured into ice–water (150 mL), neutralised and the residue was filtered off. Product **51** was purified by dissolution in DMF and subsequent precipitation with 2 *N* NaOH solution. After repetition of this procedure, **51** was obtained as orange particles (0.33 g, 41 %).

UV/vis (DMSO, 2.505 mg/10 mL): λ_{max} (a.u.) = 262 nm (0.3847), 300 (0.296 sh), 426 (0.271 sh), 476 (0.367).

Poly(vinyl{3–[3–(4–hydroxinaphthylazo]sulphonophenylpropanal}*co*-vinyl alcohol *co*-ethylen) (**52**)

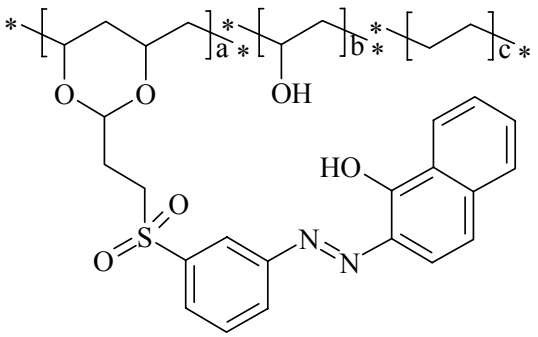


52

The polymer-dye **52** was obtained as described above: 0.15 g (0.41 mmol) of aldehyde **45** and 0.53 g (13.4 mmol, cons. 9.65 mmol OH–groups) PVA *co*-PE (27 mol %) were dissolved in 30 mL of DMF at 75 °C. 2 mL of conc HCl was added, and the reaction was carried out for 4.5 h. Purification as described for conjugates **50** and **51** provided product **52** as deep orange polymer (0.60 g, 87 %).

UV/vis (DMSO, 3.036 mg/10 mL): λ_{max} (a.u.) = 251 nm (0.314), 256 (0.352), 279 (0.320), 468 (0.298), 558 (0.707).

Poly(vinyl{3–[3–(1–hydroxinaphth–2–ylazo]sulphonophenylpropanal}*co*-vinyl alcohol *co*-ethylen) (**53**)

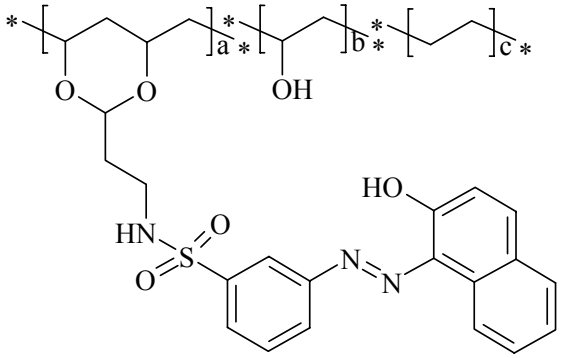


53

The synthesis of **53** succeeded according to **G. Pr. 4.2.5**. 0.40 g (10.1 mmol, 7.28 mmol OH–groups) of PVA *co*-PE (27 mol %) was dissolved in 25 mL of DMF and a solution of 0.02 g (0.054 mmol) of dye **46** in 2.0 mL of DMF was added. The reaction solution was heated to 75 °C and 1 mL of conc. HCl was added. After 2 h the reaction was cooled to 30 °C and poured into 100 mL of ice–water. The acid was neutralised and the polymer filtered off. Composite **53** was purified as described for **50** and afforded orange–red particles (0.35 g, 83 %).

UV/vis (DMSO, 5.075 mg/10 mL): λ_{max} (a.u.) = 251 nm (0.331), 257 (0.481), 320 (0.366), 535 (0.768).

Poly(vinyl{3–[3–(1–hydroxinaphth–2–ylazo]sulphonamidophenylpropanal}*co*-vinyl alcohol *co*-ethylen) (**54**)



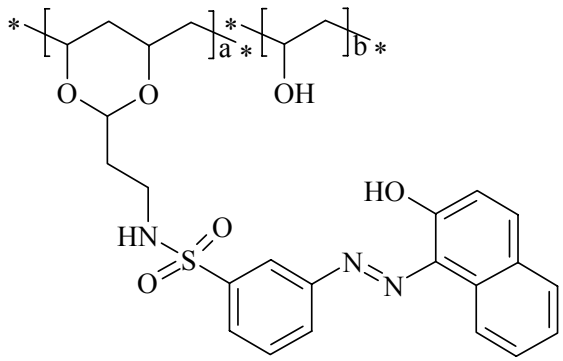
54

Polymer **54** was prepared as described above. 0.30 g (0.80 mmol) of dye **47** and 0.55 g (13.9 mmol, contain app. 10.0 mmol OH–groups) PVA *co*-PE (27 mol %) were dissolved in 25 mL of DMF and 3 mL of conc. HCl was added. The reaction was conducted at 80 °C for

2.5 h. Purification as described above afforded the orange coloured polymer **54** (0.52 g, 61 %).

UV/vis (DMSO, 1.100 mg/10 mL): λ_{max} (a.u.) = 252 nm (0.683), 260 (0.803), 477 (0.793).

Poly(vinyl{3–[3–(1–hydroxinaphth–2–ylazo]sulphonamidophenylpropanal}*co*-vinyl alcohol) (**55**)

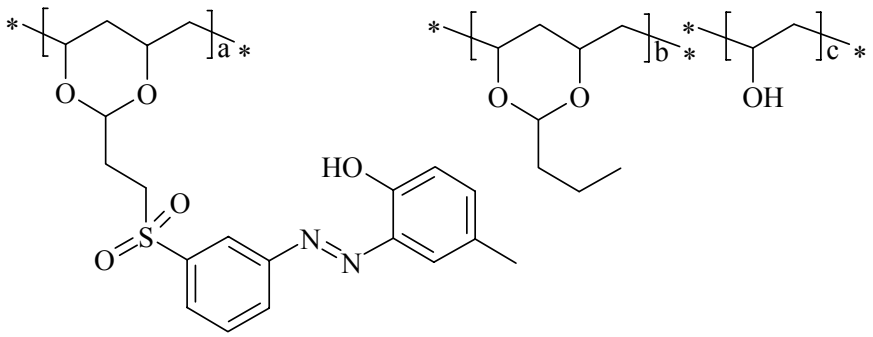


55

Dye **47** was connected to the PVA (88 % hydrolysed, Mw= 31 000– 50 000) according to ref.[58d] 0.5 g. (contain. 10.0 mmol free OH– groups) of PVA was dissolved in a mixture of 15 mL of water, 5 mL of EtOH and 2 mL of 10 % H_2SO_4 at 65 °C. 0.45 g (1.17 mmol) of aldehyde **47** was dissolved in 3 mL of DMF and was added dropwise under vigorous stirring. The temperature was increased to 75 °C and 1 mL of 50 % H_2SO_4 was added dropwise. After 2 h the polymer began to precipitate. After cooling, the reaction mixture was neutralised, diluted with 100 mL of water and placed in the refrigerator overnight. The suspension was decanted and centrifuged for 15 min at 10 000 rpm. The resulting polymer was filtered, washed with water, and dried *in vacuo*. Product **55** was obtained as a deeply orange coloured polymer (0.5 g, 51 %).

UV/vis (DMSO, 1.097 mg/10 mL): λ_{max} (a.u.) = 259 nm (1.109), 303 (0.779), 477 (1.425).

Poly(vinyl{3–[3–(2–hydroxy–5–methyl)phenylazo]sulphonophenylpropanal}*co*-vinyl butyral *co*-vinyl alcohol) (**56**)

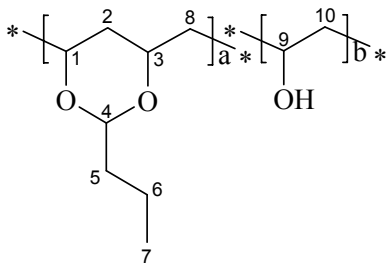


56

2.5 g PVA (Mw = 31 000–50 000, 88 % hydrolysed, contains approximately 50.0 mmol free hydroxyl groups) was dissolved in a mixture of 50 mL of water and 40 mL of EtOH at 60 °C. 0.16 g (0.50 mmol) of **19** was dissolved in 2 mL of DMF and added. 4 mL of 10 % H_2SO_4 was added and the solution was stirred for 1 h at 70 °C. 4 mL butanal was added slowly and additional 2 mL 50 % H_2SO_4 was added to the reaction mixture. During the next hour the polymer precipitated. After cooling it was filtered off and washed subsequently with water, 5 % NaOH solution and again with water. Purification was achieved by dissolution in THF and subsequent precipitation with water. The procedure was repeated. Product **56** was obtained as orange coloured polymer (no moving dyes spots on TLC), yield 1.72 g (65 %).

UV/vis (DMSO, 7.170 mg/10 mL): λ_{max} (a.u.) = 258 nm (0.836), 283 (0.836), 316 (0.633 sh), 399 (0.319).

Poly(vinyl alcohol *co* ca. 30 mol % vinylbutytal) (**123**)



123

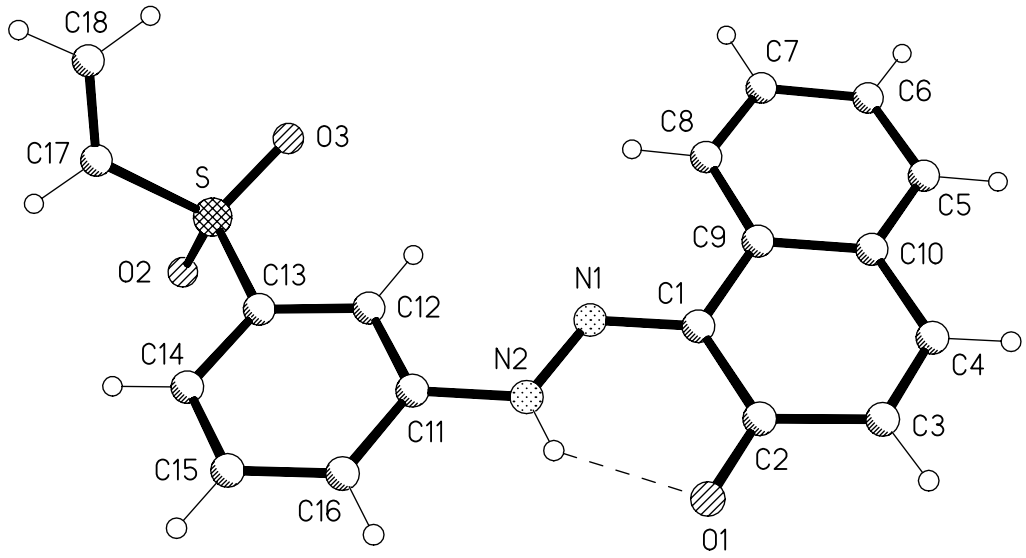
The synthesis of the polymer was carried out according to Alaimo.[18] 5.0 g of poly(vinyl alcohol) (Mw = 22 000, 88 % hydrolyzed), containing approximately 102 mmol free hydroxyl groups was dissolved in 100 mL of 30 % (v/v) of aqueous ethanolic solution

and the mixture was heated to 70 °C. 2 mL of 10 % H_2SO_4 was added. 1.10 g (15.3 mmol) of butanal was dissolved in 10 mL of ethanol and, the solution added dropwise into reaction mixture during 5 min. Additional 1 mL of 50 % H_2SO_4 was added and the solution was stirred at that temperature for 1 h. After 20 min the product started to precipitate. The reaction mixture was allowed to cool to room temperature and was poured into 200 mL of water, the precipitate was collected and dried. The product was purified by redissolving in 120 mL of THF and precipitation with 200 mL of water. Polymer **123** was centrifuged, filtered and dried *in vacuo* at 70 °C (5.0 g, 80 %).

^{1}H NMR (DMSO–d_6, 200.133 MHz): δ = 4.67 (s, 4–H), 4.47 (s, OH), 4.21 (d, 1–, 3–H), 3.81 (s, 9–H), 2.88 (s, 5–H), 2.73 (s, 6–H), 1.35 (m, 2–, 8–, 10–H), 0.86 (t, 7–H).

6. X–ray crystal structure data

2–(3–Ethenesulphonyl–phenylazo) naphthalene–2–ol (**21**)



Empirical formula	$C_{17}H_{20}N_4O_2$	
Formula weight	312.37	
Temperature	133(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P(-1)	
Unit cell dimensions	a = 8.8477(14) Å	α= 70.563(8)°
	b = 9.5975(16) Å	β= 80.940(8)°

	c = 10.2363(16) Å γ = 75.893(8)°
Volume	792.2(2) Å^3
Z	2
Density (calculated)	1.310 Mg/m^3
Absorption coefficient 0.089 mm^{-1}	
F(000)	332
Crystal size	0.30 x 0.18 x 0.03 mm^3
Theta range for data collection	2.12 to 30.03°
Reflections collected	9195
Independent reflections	4574 [R(int) = 0.0299]
Completeness to theta = 30.00°	98.4 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4574 / 0 / 219
Goodness-of-fit on F^2	0.954
Final R indices [I>2sigma(I)]	R1 = 0.0440, wR2 = 0.1021
R indices (all data)	R1 = 0.0770, wR2 = 0.1121
Largest diff. peak and hole	0.323 and -0.232 e.Å^{-3}

Table 6–1. Bond lengths [Å].

S–O(3)	1.4345(12)	C(5)–C(10)	1.4063(19)
S–O(2)	1.4406(12)	C(6)–C(7)	1.399(2)
S–C(17)	1.7525(15)	C(7)–C(8)	1.3847(19)
S–C(13)	1.7709(13)	C(8)–C(9)	1.3959(18)
C(17)–C(18)	1.288(3)	C(9)–C(10)	1.4177(18)
C(1)–N(1)	1.3240(16)	C(11)–C(12)	1.3949(17)
C(1)–C(9)	1.4652(17)	C(11)–C(16)	1.3962(17)
C(1)–C(2)	1.4685(17)	C(11)–N(2)	1.3978(17)
C(2)–O(1)	1.2542(16)	C(12)–C(13)	1.3932(18)
C(2)–C(3)	1.4534(19)	C(13)–C(14)	1.3904(18)
C(3)–C(4)	1.350(2)	C(14)–C(15)	1.3923(19)
C(4)–C(10)	1.4430(18)	C(15)–C(16)	1.3870(19)
C(5)–C(6)	1.383(2)	N(1)–N(2)	1.3145(15)

Table 6–2. Bond angles [°].

O(3)–S–O(2)	118.94(8)	C(8)–C(9)–C(10)	119.08(12)
O(3)–S–C(17)	108.25(7)	C(8)–C(9)–C(1)	122.10(12)
O(2)–S–C(17)	106.98(7)	C(10)–C(9)–C(1)	118.81(11)
O(3)–S–C(13)	108.21(6)	C(5)–C(10)–C(9)	119.37(12)
O(2)–S–C(13)	107.98(7)	C(5)–C(10)–C(4)	121.19(12)
C(17)–S–C(18)	105.74(7)	C(9)–C(10)–C(4)	119.44(12)
C(18)–C(17)–S	123.40(15)	C(12)–C(11)–C(16)	120.62(12)
N(1)–C(1)–C(9)	115.79(11)	C(12)–C(11)–N(2)	121.83(11)
N(1)–C(1)–C(2)	124.01(11)	C(16)–C(11)–N(2)	117.54(11)
C(9)–C(1)–C(2)	120.12(11)	C(13)–C(12)–C(11)	118.02(12)
O(1)–C(2)–C(3)	121.49(12)	C(14)–C(13)–C(12)	122.27(12)
O(1)–C(2)–C(1)	121.11(12)	C(14)–C(13)–S	119.40(10)
C(3)–C(2)–C(1)	117.39(12)	C(12)–C(13)–S	118.27(10)
C(4)–C(3)–C(2)	121.31(12)	C(13)–C(14)–C(15)	118.56(12)
C(3)–C(4)–C(10)	122.80(12)	C(16)–C(15)–C(14)	120.49(12)
C(6)–C(5)–C(10)	120.54(13)	C(15)–C(16)–C(11)	120.00(12)
C(5)–C(6)–C(7)	120.72(13)	N(2)–N(1)–C(1)	119.56(11)
C(8)–C(7)–C(6)	120.72(13)	N(1)–N(2)–C(11)	119.62(11)
C(7)–C(8)–C(9)	120.72(13)		

Table 6–3. Hydrogen bonds [Å and °].

D–H...A	d(D–H)	d(H...A)	d(D...A)	<(DHA)
N(2)–H(02)...O(1)	0.828(18)	1.920(18)	2.5719(15)	134.9(16)
C(16)–H(16)...O(1)#1	0.95	2.39	3.3304(16)	168.3
C(15)–H(15)...O(2)#2	0.95	2.43	3.3706(17)	168.9
C(7)–H(7)...O(3)#3	0.95	2.61	3.5489(19)	170.6

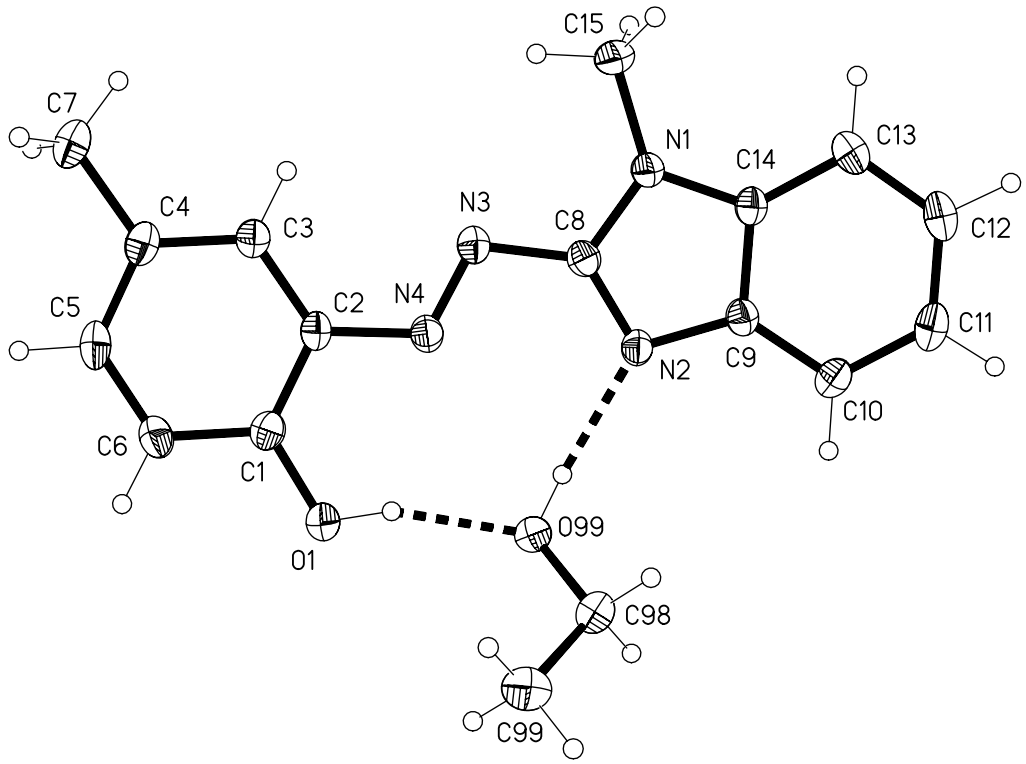
Symmetry transformations used to generate equivalent atoms:

#1 –x+1,–y,–z+1

#2 –x+1/2,y+1/2,–z+1/2

#3 –x+1,–y,–z

Methyl–2–(1–methylbenzimidazol–2–ylazo) phenol (**122**)



Empirical formula	$C_{17}H_{20}N_4O_2$	
Formula weight	312.37	
Temperature	133(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P(–1)	
Unit cell dimensions	a = 8.8477(14) Å	α= 70.563(8)°
	b = 9.5975(16) Å	β= 80.940(8)°
	c = 10.2363(16) Å	γ = 75.893(8)°
Volume	792.2(2) $Å^3$	
Z	2	

Density (calculated)	1.310 Mg/m^3
Absorption coefficient	0.089 mm^{-1}
F(000)	332
Crystal size	0.30 x 0.18 x 0.03 mm^3
Theta range for data collection	2.12 to 30.03°
Reflections collected	9195
Independent reflections	4574 [R(int) = 0.0299]
Completeness to theta = 30.00°	98.4 %
Absorption correction	None
Refinement method	Full–matrix least–squares on F^2
Data / restraints / parameters	4574 / 0 / 219
Goodness–of–fit on F^2	0.954
Final R indices [I>2sigma(I)]	R1 = 0.0440, wR2 = 0.1021
R indices (all data)	R1 = 0.0770, wR2 = 0.1121
Largest diff. peak and hole	0.323 and –0.232 e.Å^{-3}

Table 6–4. Bond lengths [Å]

C(1)	O(1)	1.3542(15)	C(9)	N(2)	1.3839(16)
C(1)	C(6)	1.3985(17)	C(9)	C(10)	1.3981(17)
C(1)	C(2)	1.4032(17)	C(9)	C(14)	1.4095(17)
C(2)	N(4)	1.3984(16)	C(10)	C(11)	1.3817(19)
C(2)	C(3)	1.4039(17)	C(11)	C(12)	1.398(2)
C(3)	C(4)	1.3830(17)	C(12)	C(13)	1.3770(19)
C(4)	C(5)	1.4039(18)	C(13)	C(14)	1.3949(18)
C(4)	C(7)	1.5074(18)	C(14)	N(1)	1.3769(16)
C(5)	C(6)	1.3767(18)	C(15)	N(1)	1.4575(16)
C(8)	N(2)	1.3249(15)	N(3)	N(4)	1.2688(14)
C(8)	N(1)	1.3691(15)	C(98)	O(99)	1.4224(16)
C(8)	N(3)	1.3995(16)	C(98)	C(99)	1.503(2)

Table 6–5. Bond angles [°].

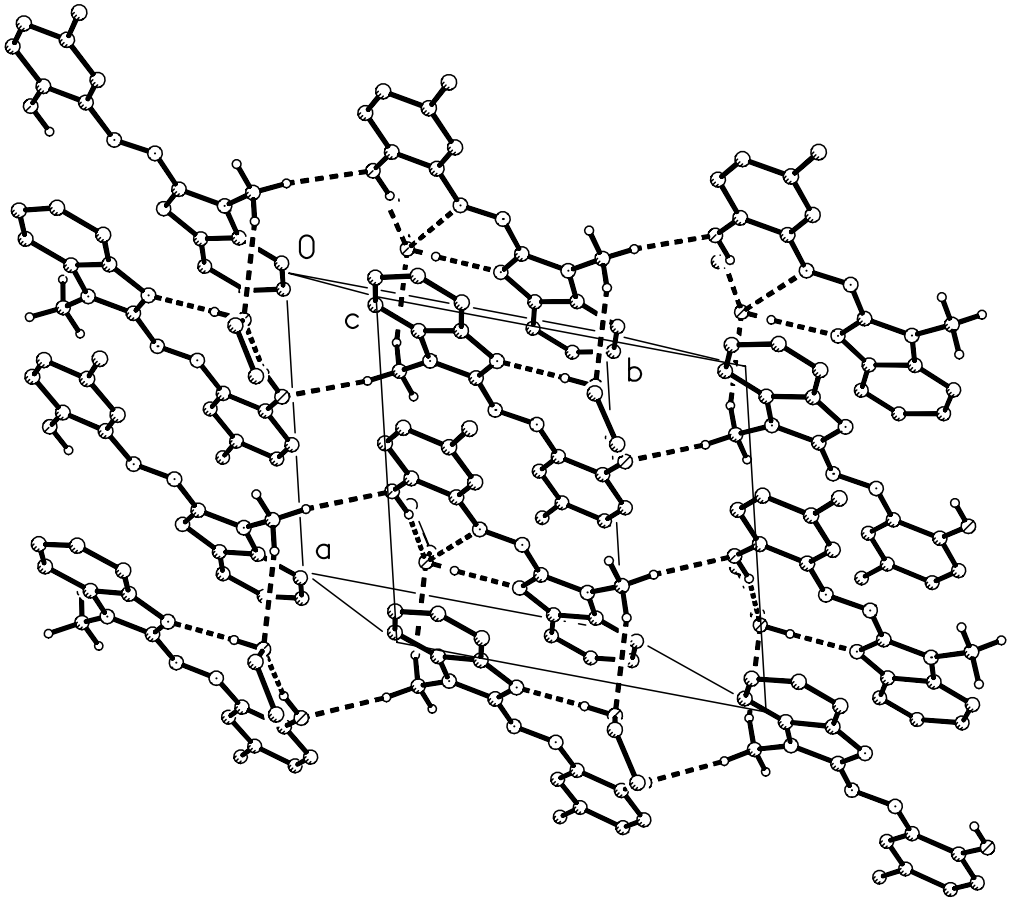
O(1)–C(1)–C(6)	117.69(12)	N(2)–C(9)–C(14)	110.05(11)
O(1)–C(1)–C(2)	123.47(11)	C(10)–C(9)–C(14)	119.93(11)
C(6)–C(1)–C(2)	118.83(12)	C(11)–C(10)–C(9)	117.61(12)
N(4)–C(2)–C(1)	114.44(11)	C(10)–C(11)–C(12)	121.56(13)
N(4)–C(2)–C(3)	125.45(12)	C(13)–C(12)–C(11)	122.14(12)
C(1)–C(2)–C(3)	120.11(11)	C(12)–C(13)–C(14)	116.41(13)
C(4)–C(3)–C(2)	121.23(12)	N(1)–C(14)–C(13)	131.97(12)
C(3)–C(4)–C(5)	117.56(12)	N(1)–C(14)–C(9)	105.63(10)
C(3)–C(4)–C(7)	121.88(12)	C(13)–C(14)–C(9)	122.34(12)
C(5)–C(4)–C(7)	120.55(12)	C(8)–N(1)–C(14)	106.25(10)
C(6)–C(5)–C(4)	122.40(12)	C(8)–N(1)–C(15)	127.52(10)
C(5)–C(6)–C(1)	119.84(12)	C(14)–N(1)–C(15)	126.23(11)
N(2)–C(8)–N(1)	113.67(11)	C(8)–N(2)–C(9)	104.38(10)
N(2)–C(8)–N(3)	127.98(11)	N(4)–N(3)–C(8)	110.91(10)
N(1)–C(8)–N(3)	118.34(11)	N(3)–N(4)–C(2)	116.28(10)
N(2)–C(9)–C(10)	130.00(12)	O(99)–C(98)–C(99)	111.00(12)

Table 6–6. Hydrogen bonds [Å and °].

D–H...A	d(D–H)	d(H...A)	d(D...A)	<(DHA)
O(1)–H(01)...O(99)	0.883(19)	1.88(2)	2.7288(14)	161.4(17)
O(99)–H(99)...N(2)	0.877(18)	1.922(18)	2.7957(15)	174.5(16)
O(99)–H(99)...N(4)	0.877(18)	2.546(17)	2.9822(15)	111.6(13)
C(15)–H(15B)...O(1)#1	0.98	2.56	3.5318(18)	172.7
C(15)–H(15A)...O(99)#2	0.98	2.65	3.4923(18)	143.7

Symmetry transformations used to generate equivalent atoms: #1 x,y–1,z; #2 –x,–y+1,–z+1

Package picture of **122**:



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